Electronic Supplementary Information

Effect of fluorine substitution of the *β*-ketoiminate ancillary ligand on photophysical properties and electroluminescent ability of new iridium(III) complexes

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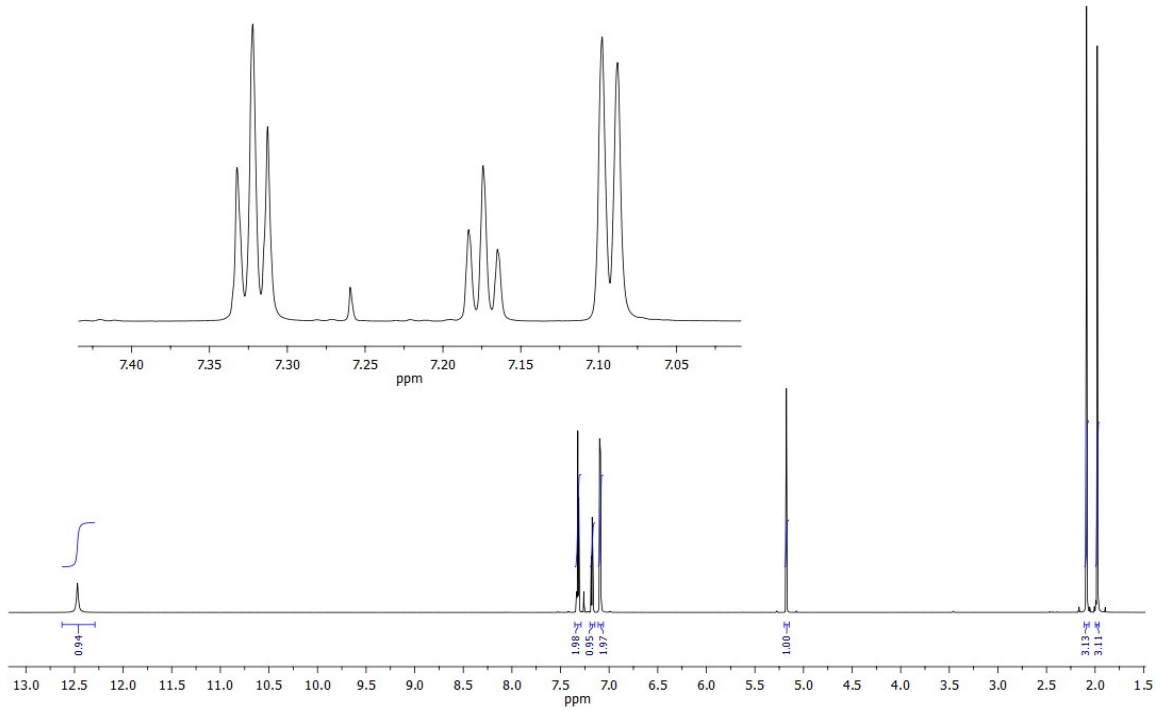
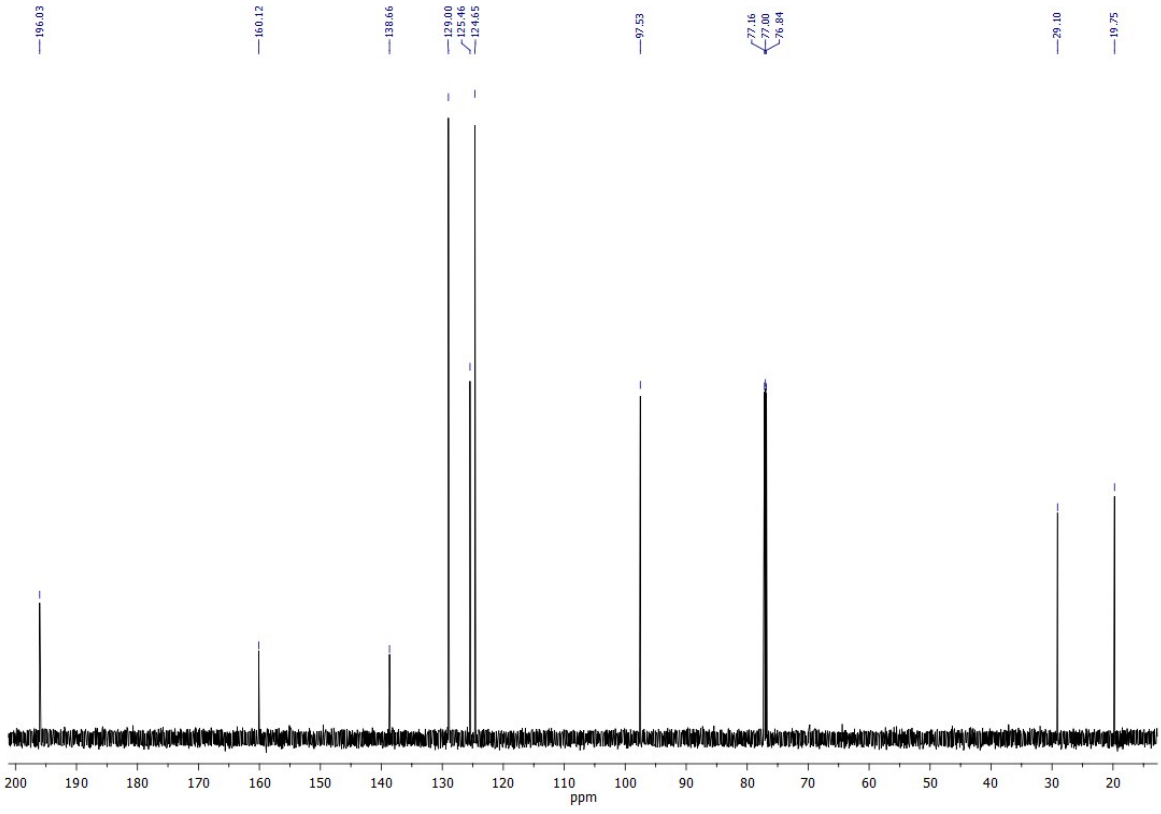
1. Spectroscopic data of 4-arylimino-2-pentanones

4-Phenylimino-2-pentanone (3a)





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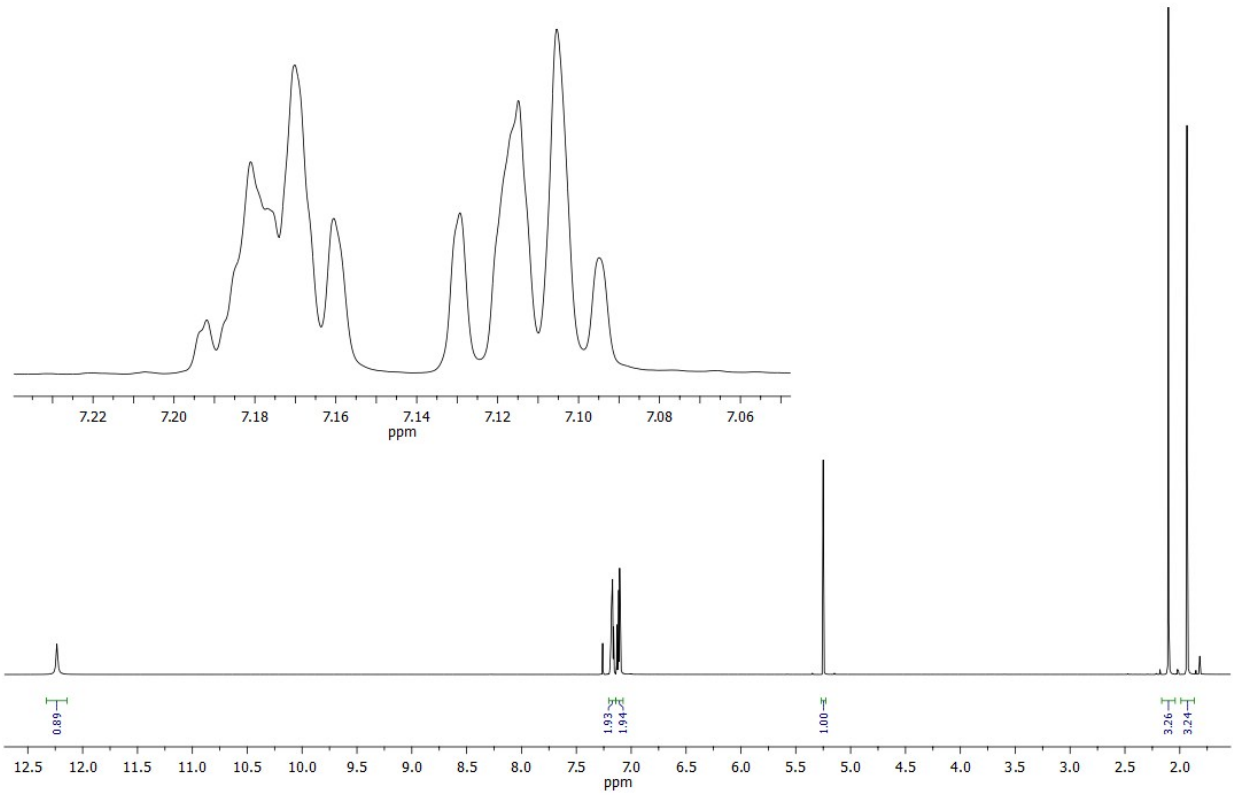

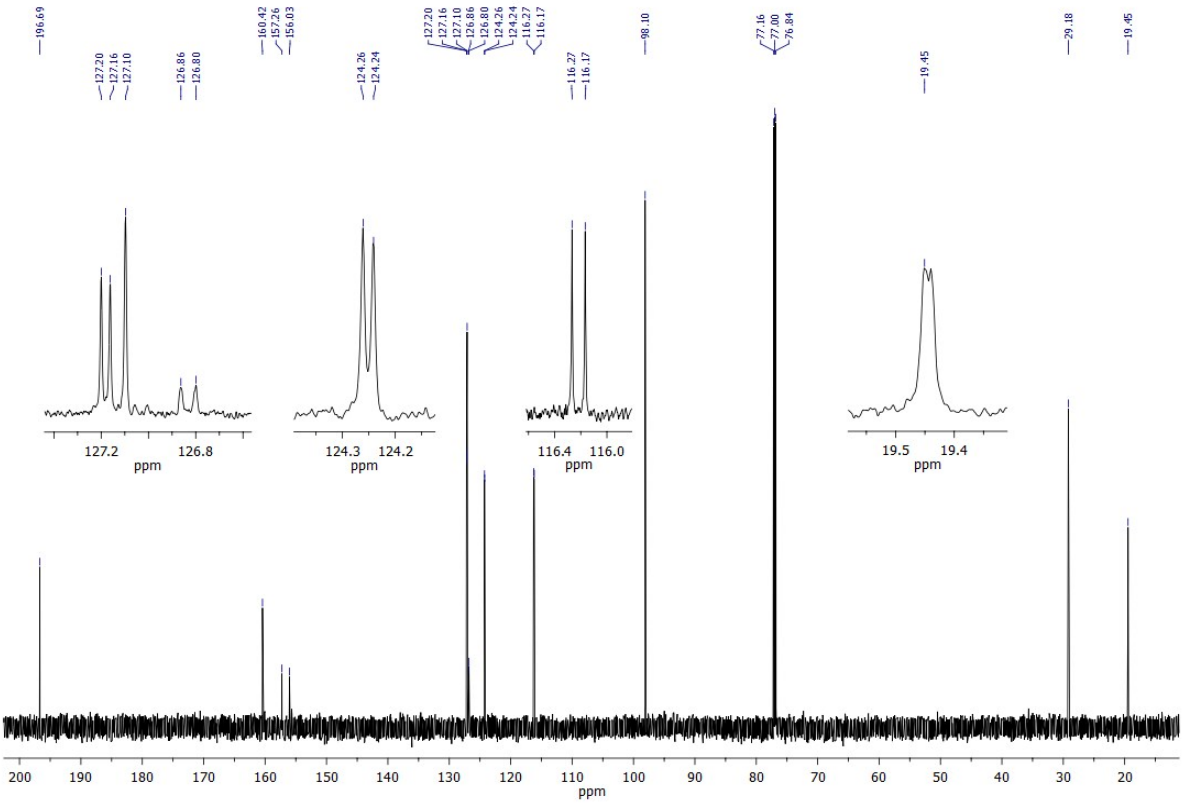

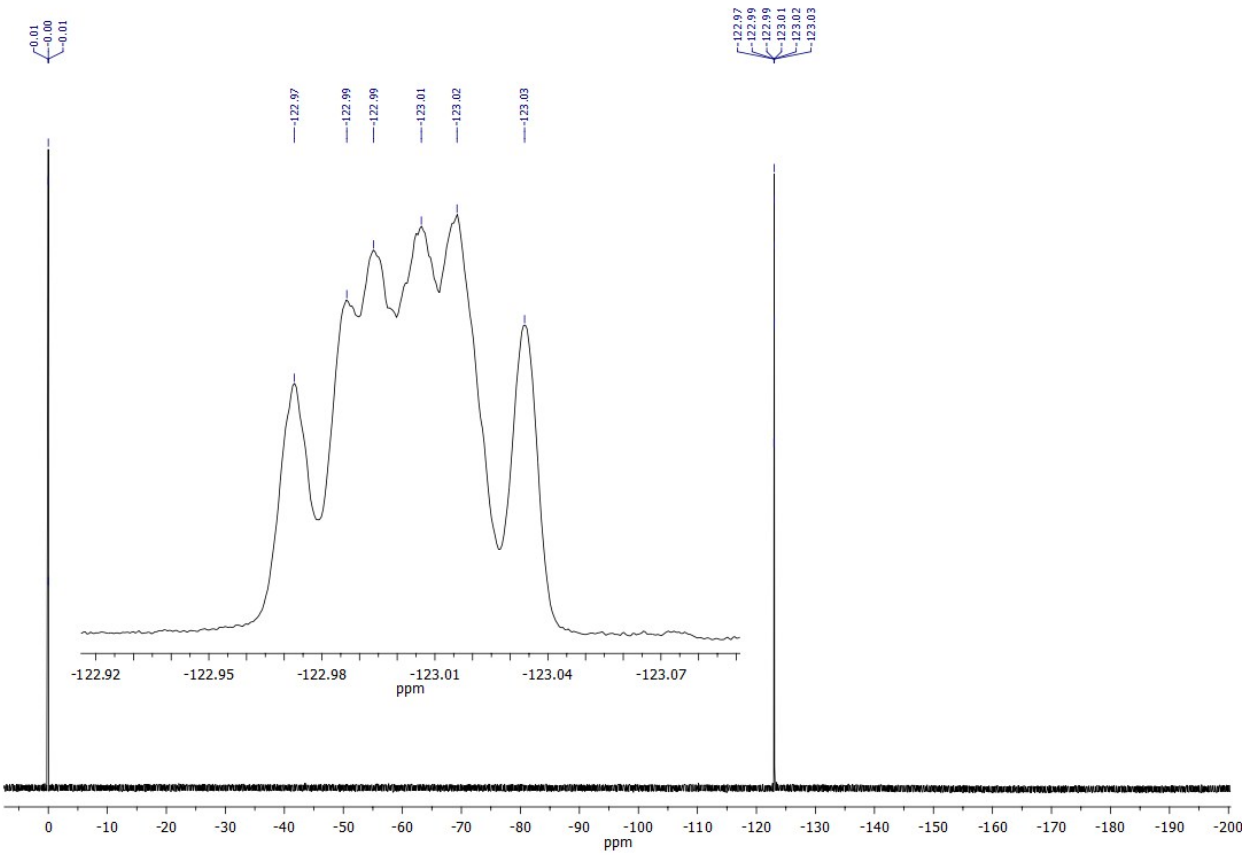
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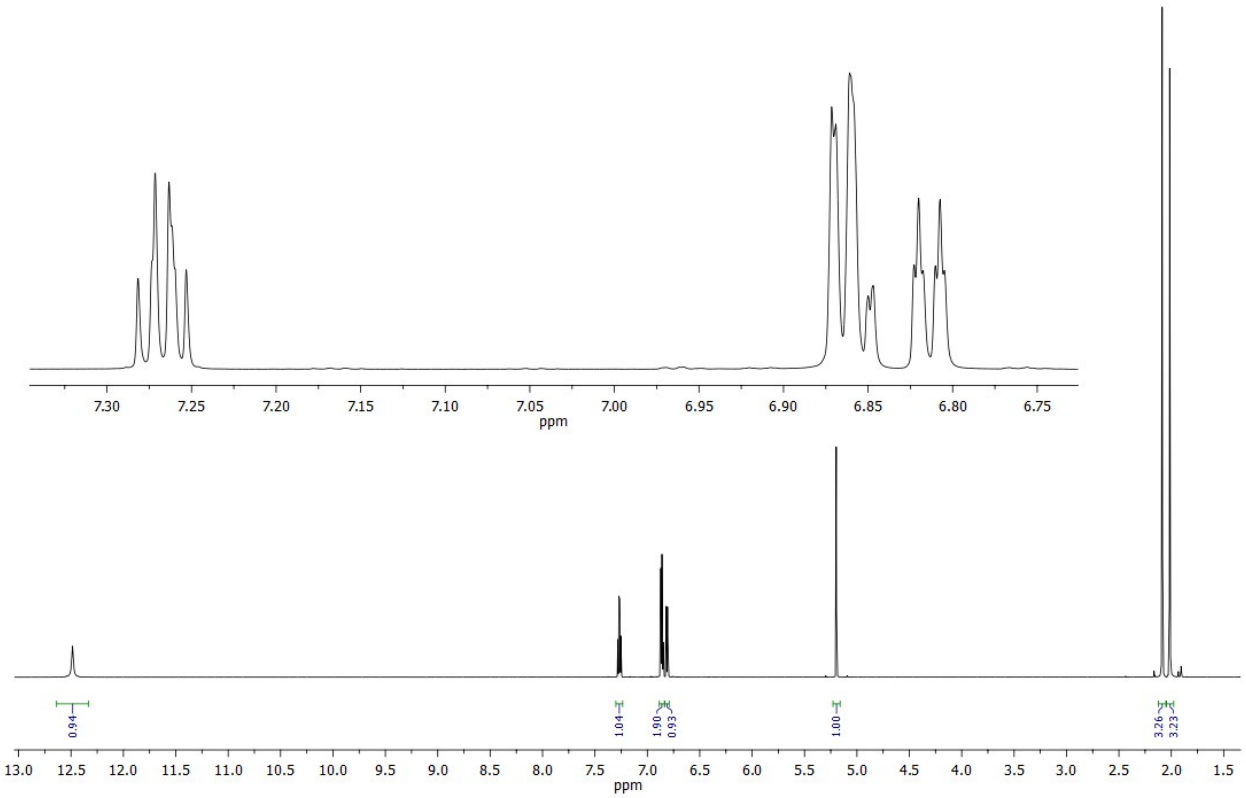

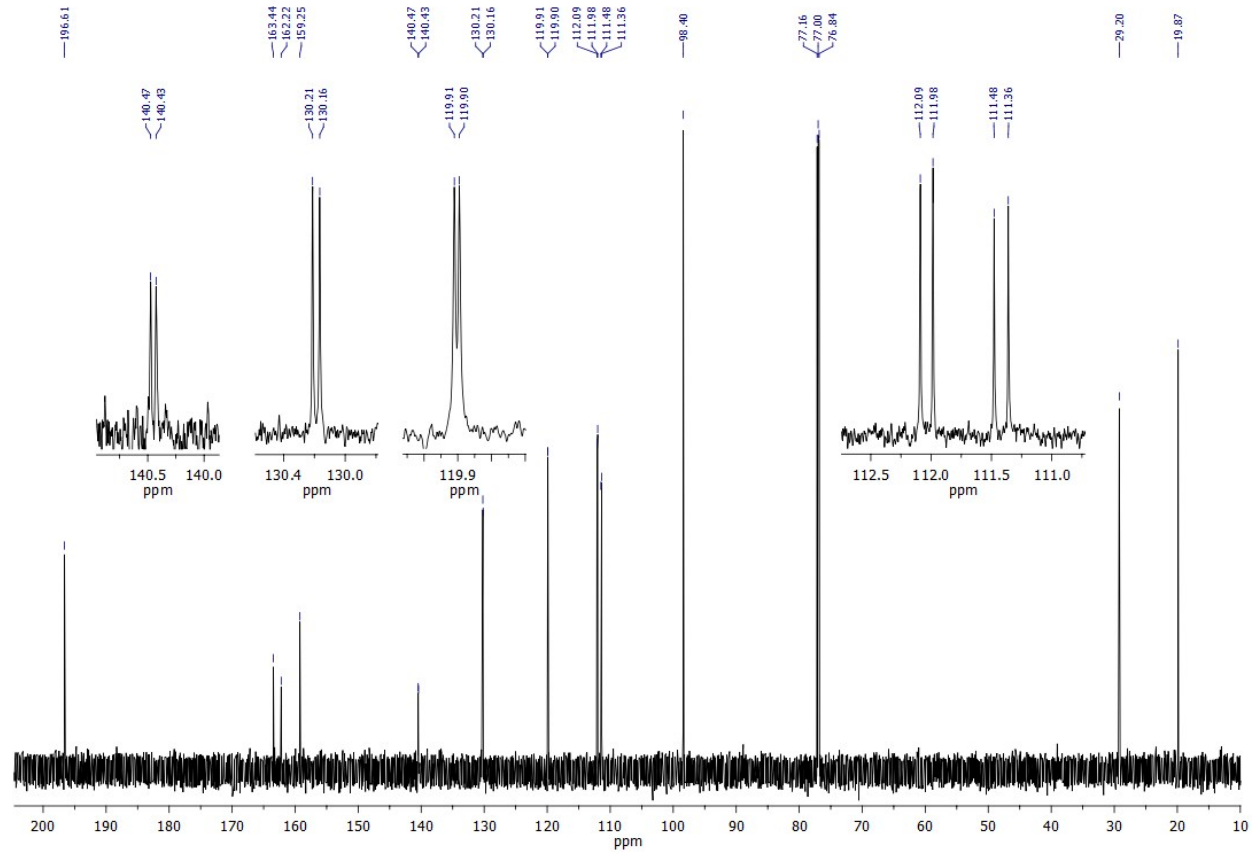

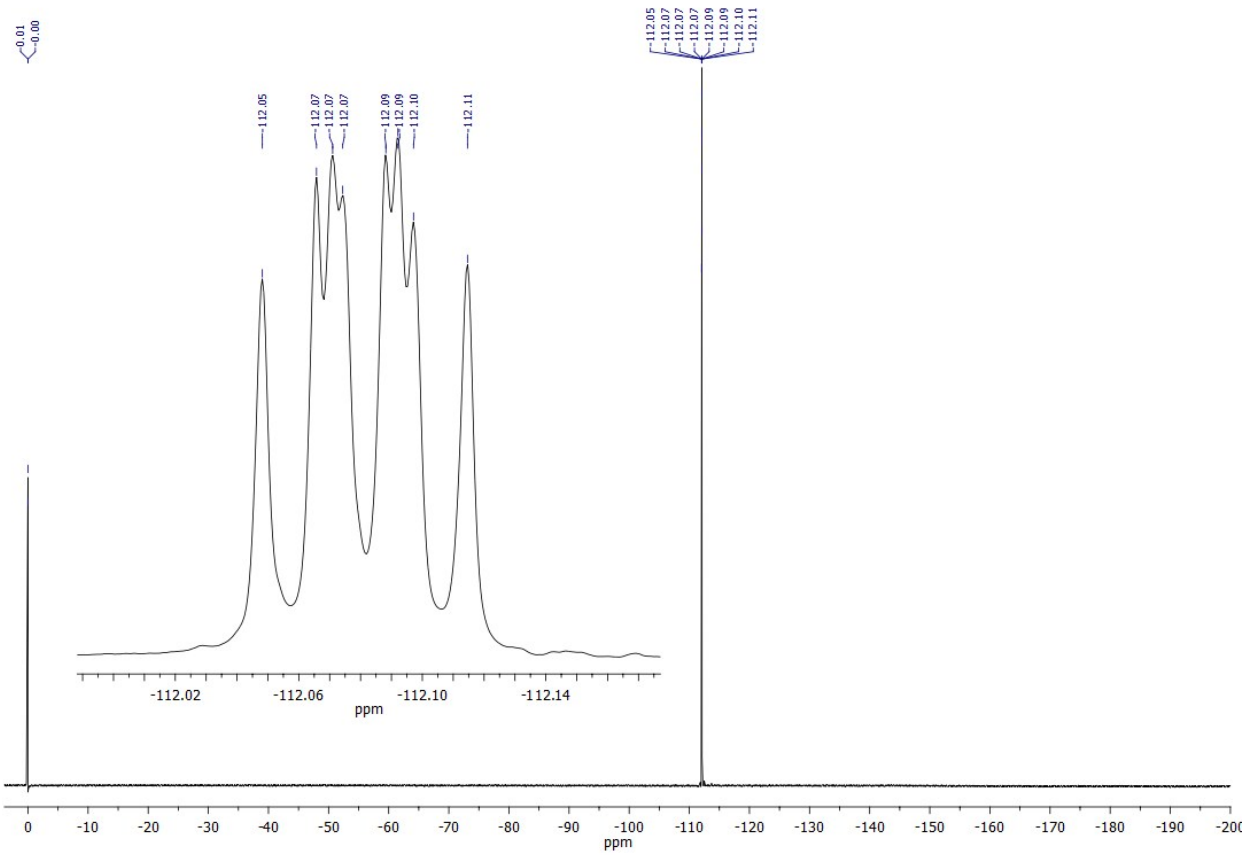
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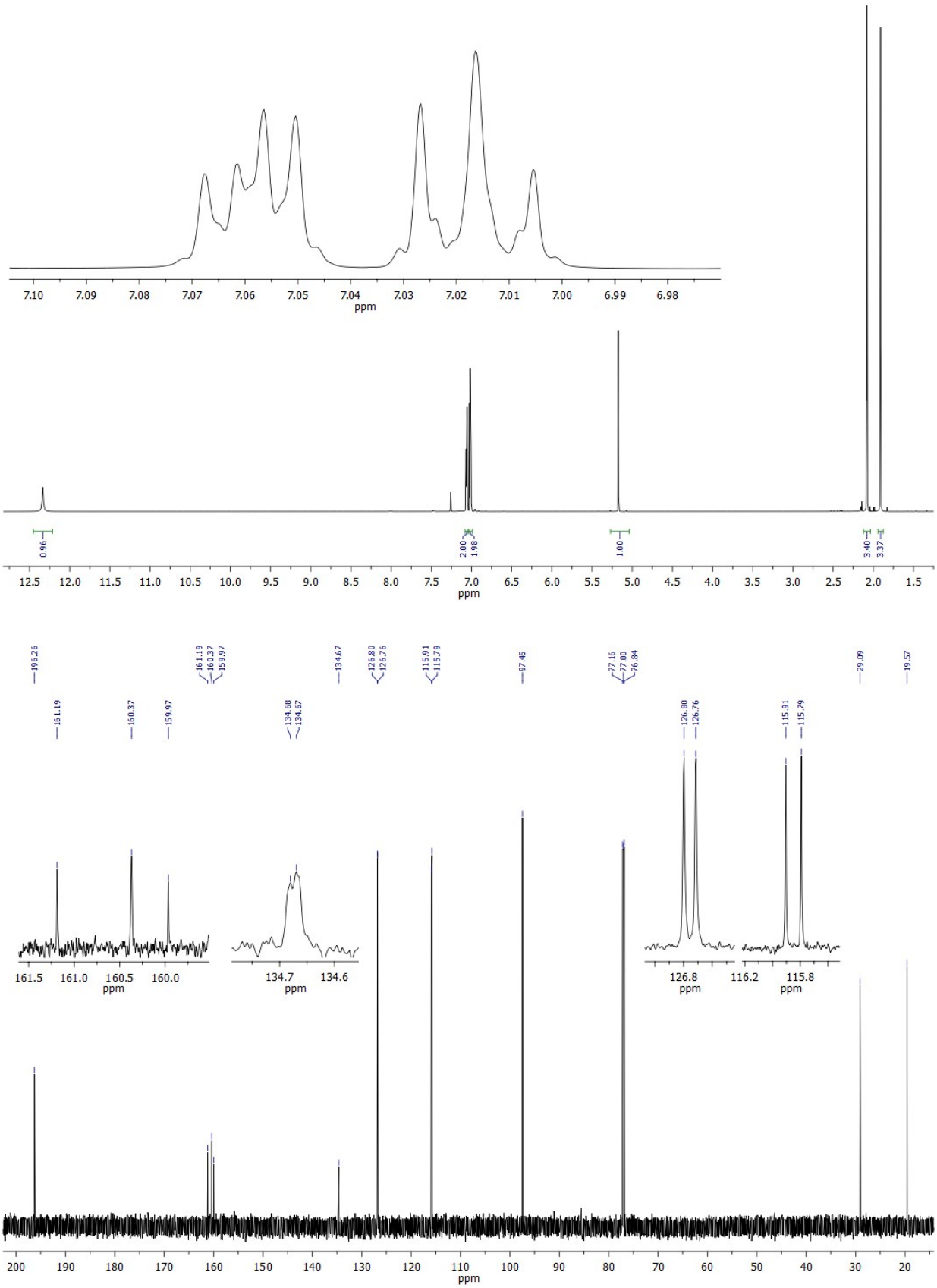

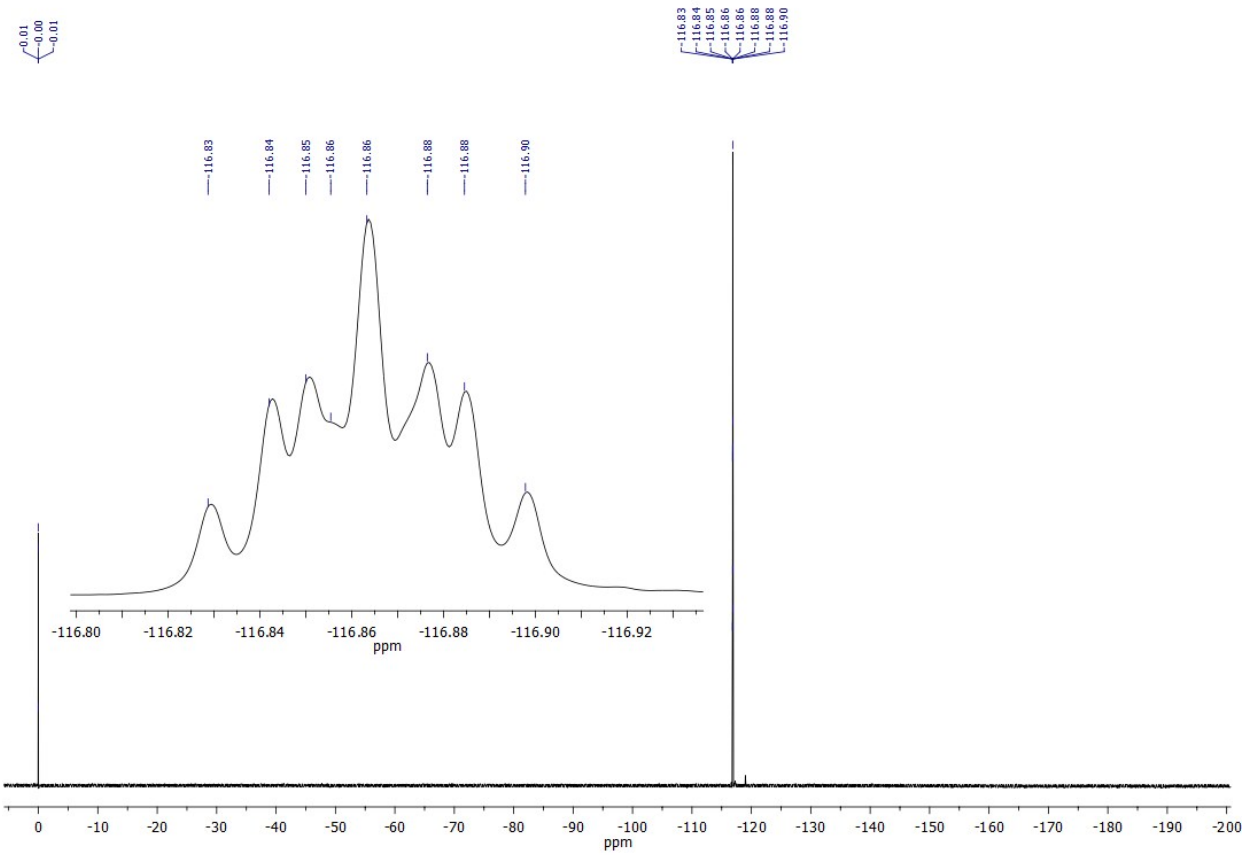
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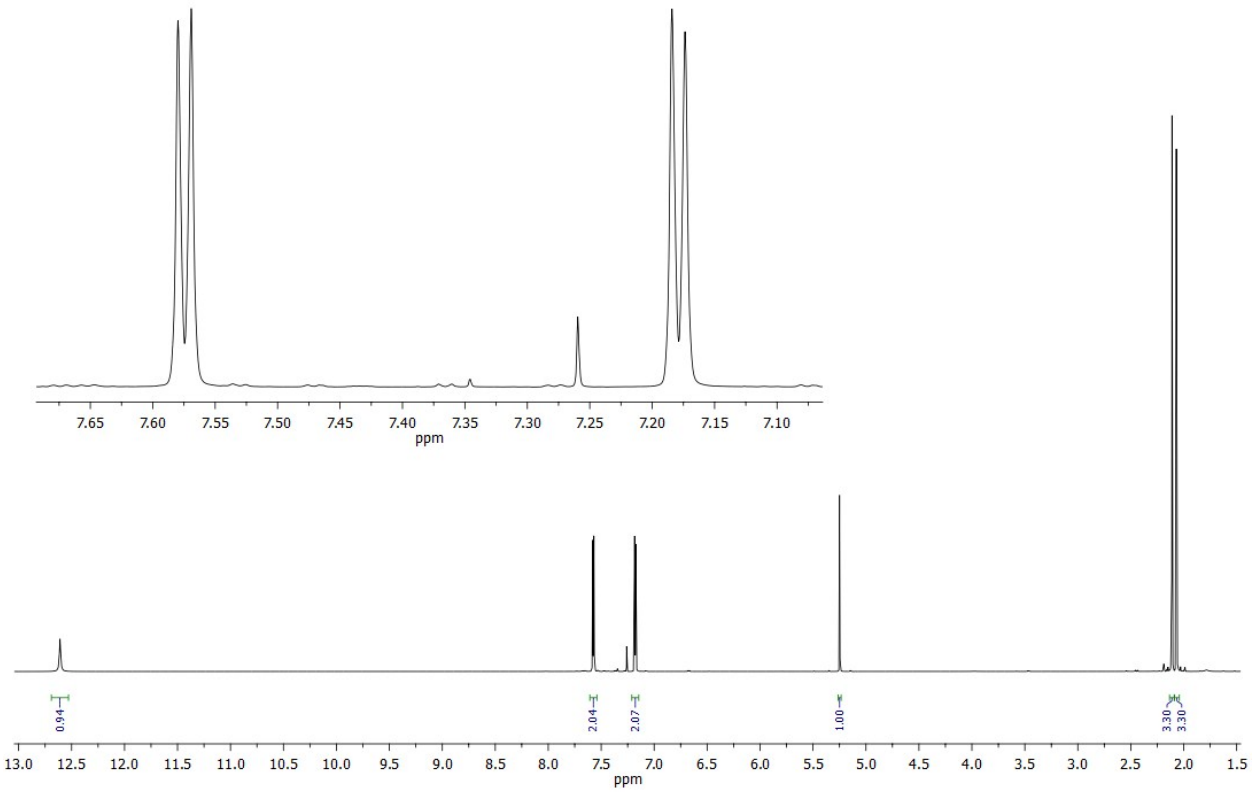

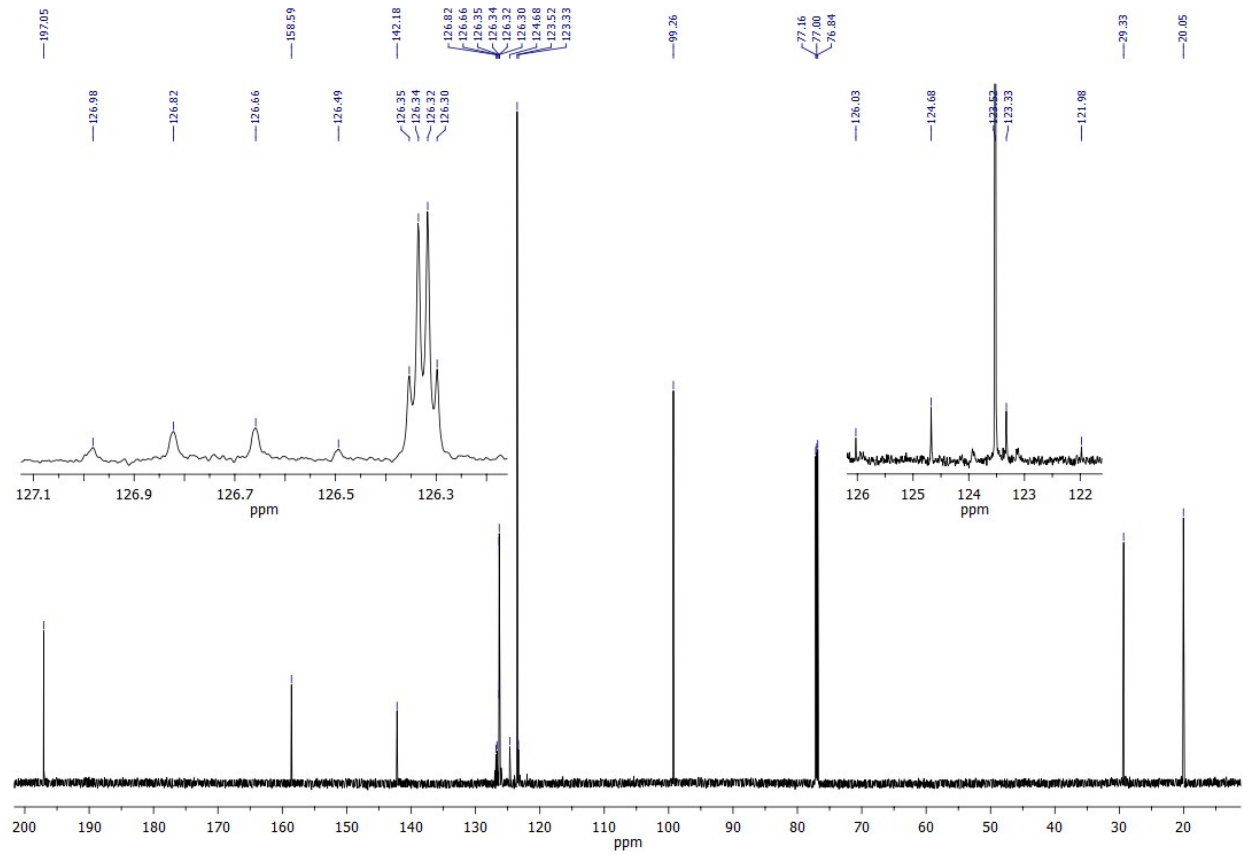

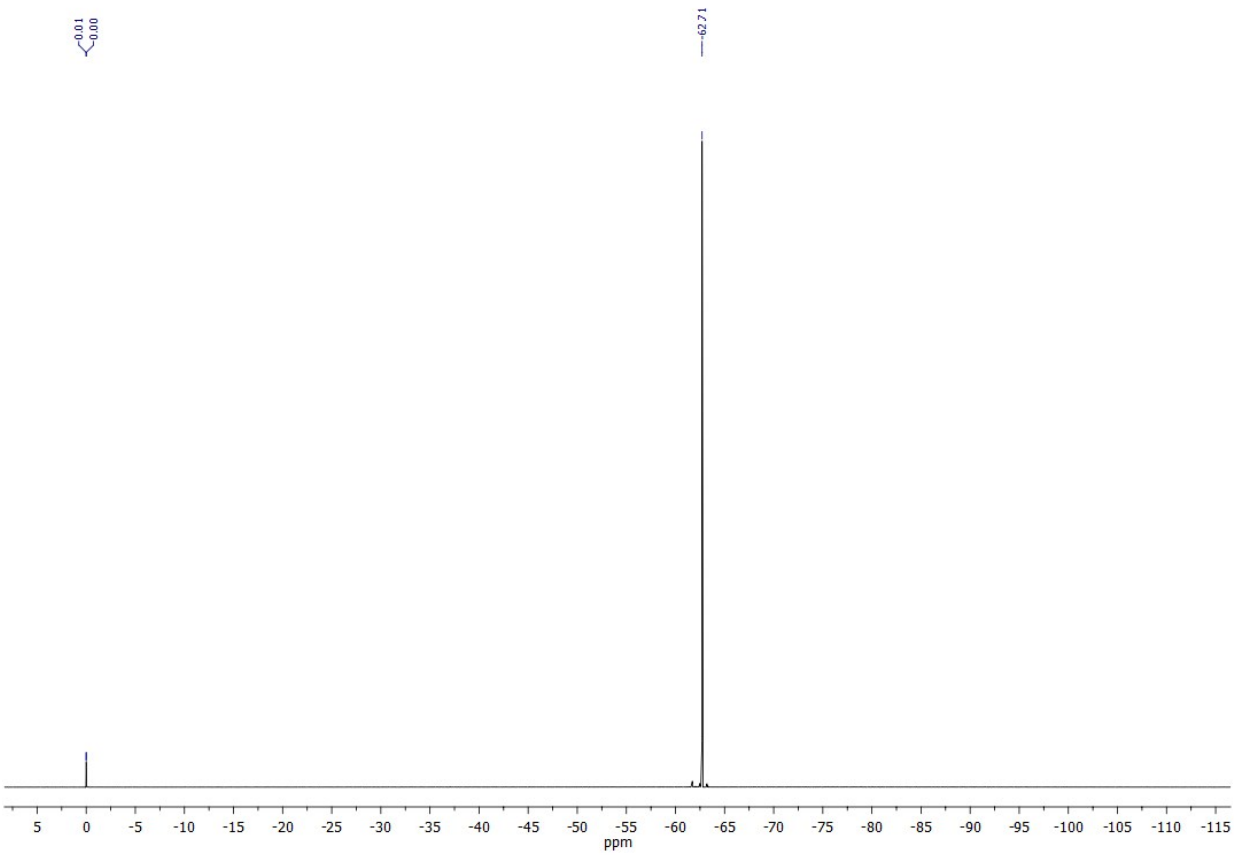
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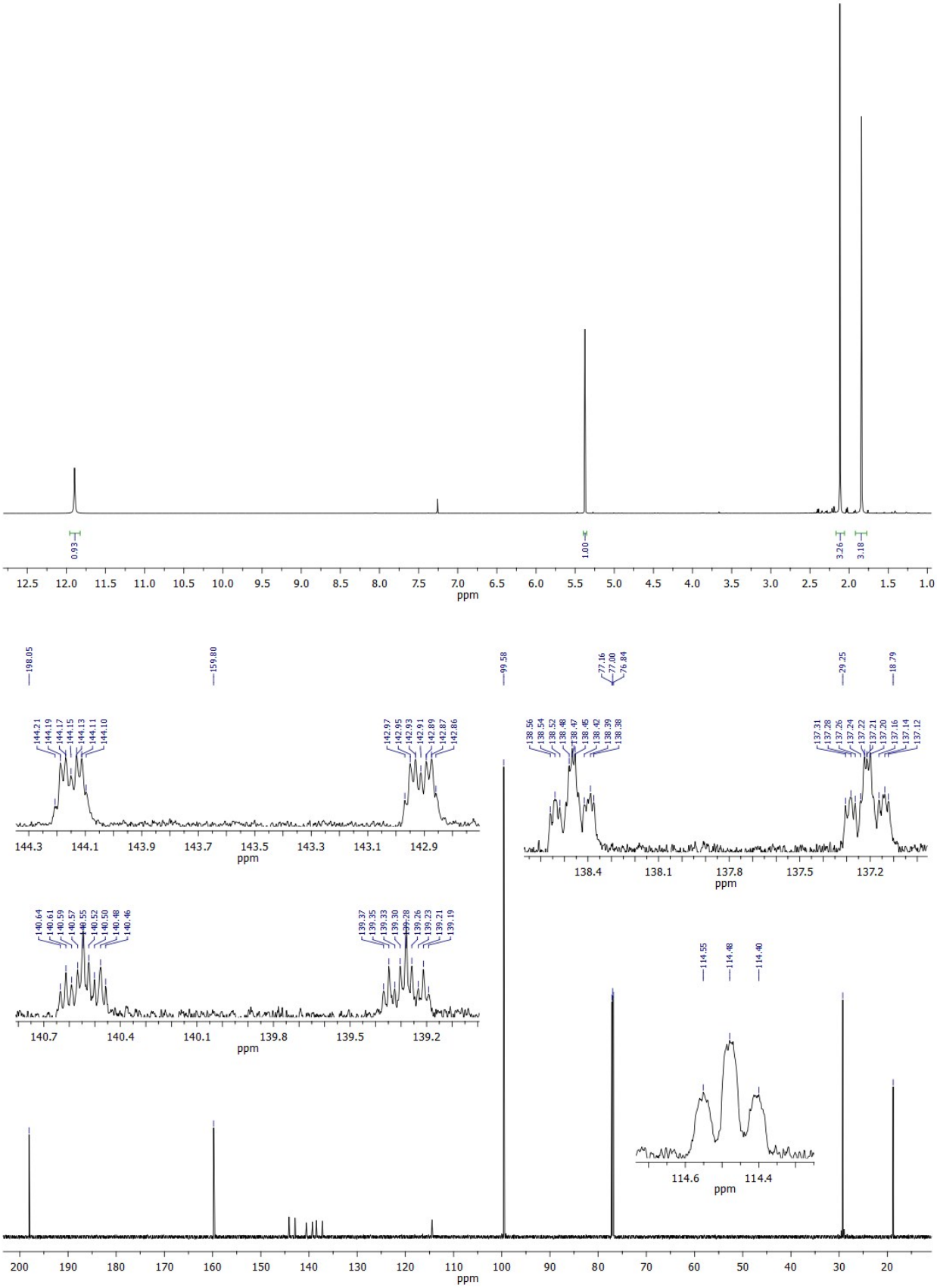
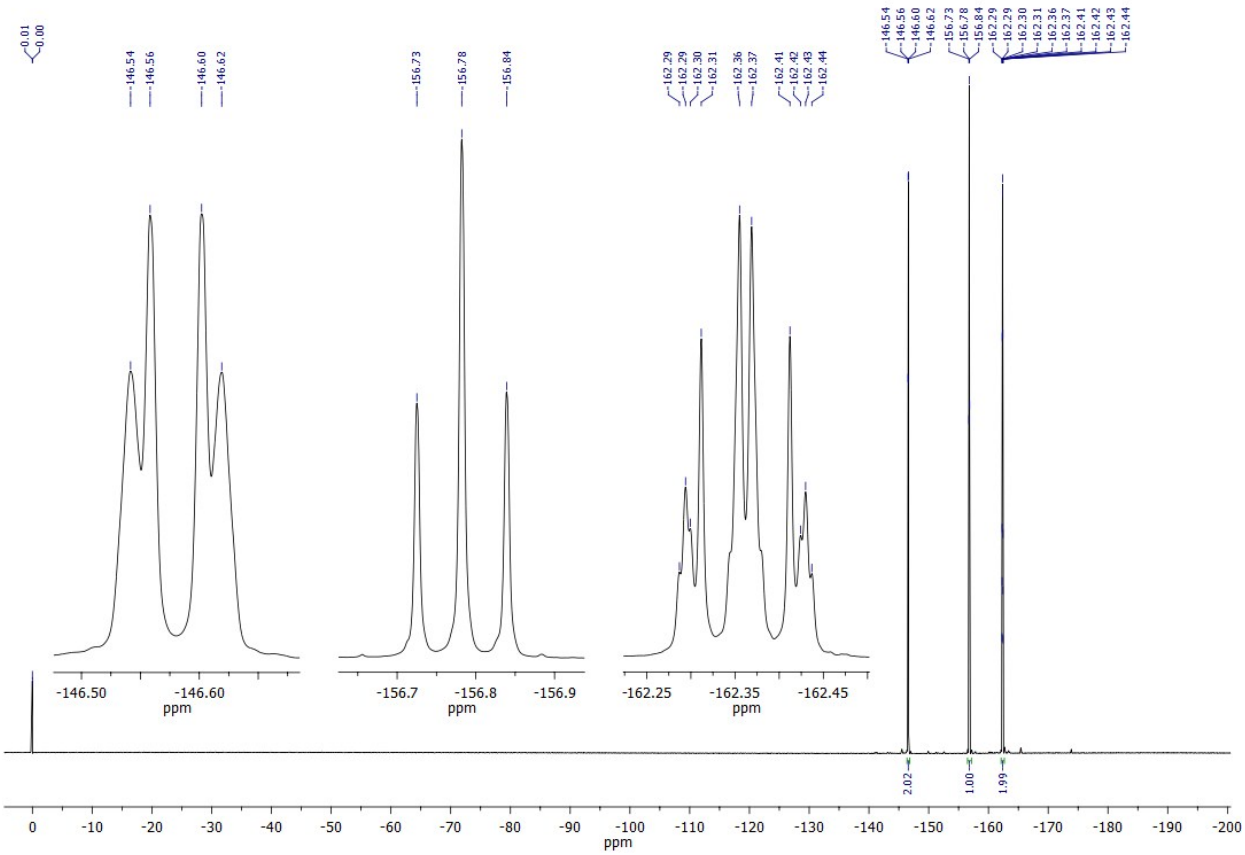
4-(2,3,4,5,6-Pentafluorophenyl)imino-2-pentanone (3f)

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-190
-200
ppm

2. Crystallographic data

Table 1S. Crystal data, data collection and structure refinement

Compound	**3f**	**5b**	**5e**	**5g**
Formula	$C_{11}H_8F_5NO$	$C_{37}H_{27}FIrN_3O$	$C_{38}H_{27}F_3IrN_3O_2 \cdot 1/2(CH_3OH)$	$C_{40}H_{30}F_4IrN_3O$
Formula weight	265.18	740.81	806.85	868.87
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	C2/c	I2/a
a(Å)	10.8061(4)	16.3067(4)	27.6629(10)	16.4734(6)
b(Å)	8.7128(3)	18.7491(4)	9.1355(2)	12.7322(5)
c(Å)	11.6109(4)	19.7051(5)	29.0965(11)	31.2845(11)
α(°)	90	90	90	90
β(º)	90.422(3)	108.847(3)	117.344(5)	99.973(3)
γ(°)	90	90	90	90
V(Å^3)	1093.15(7)	5701.5(3)	6531.5(5)	6462.5(4)
Z	4	8	8	8
D_x(g cm^{-3})	1.61	1.73	1.64	1.79
F(000)	536	2912	3176	3424
μ(mm^{-1})	0.16	4.73	4.14	4.20
Θ range (^{0})	3.47 – 27.03	3.06 – 26.52	3.06 – 27.01	2.95 – 28.31
Reflections:				
collected	7398	24228	14409	14925
unique (R_{int})	2234 (0.014)	10919 (0.037)	6545 (0.022)	6750 (0.021)
with I>2σ(I)	2042	8514	5874	5971
R(F) [I>2σ(I)]	0.032	0.047	0.035	0.026
wR(F^2) [I>2σ(I)]	0.084	0.094	0.100	0.068
R(F) [all data]	0.036	0.067	0.041	0.033
wR(F^2) [all data]	0.086	0.102	0.105	0.072
Goodness of fit	1.05	1.05	1.07	1.01
max/min Δρ (e Å^{-3})	0.20/-0.20	2.87/-1.81	1.16/-0.85	2.09/-1.06

Table 2S. Hydrogen bond data (Å, °)

D	H	A	D-H	H···A	D···A	D-H···A
3f						
N7	H7	O10	0.881(18)	1.978(17)	2.6669(14)	134.0(15)
N7	H7	O10^{i}	0.881(18)	2.293(18)	2.9749(14)	134.1(14)
C81	H81A	F2	0.96(2)	2.431(19)	3.0451(17)	121.2(14)
C81	H81A	F2^{ii}	0.96(2)	2.53(2)	3.2224(16)	128.3(14)

Symmetry codes: ^{i} 1-x,1-y,1-z; ^{ii} 1-x,1-y,-z;

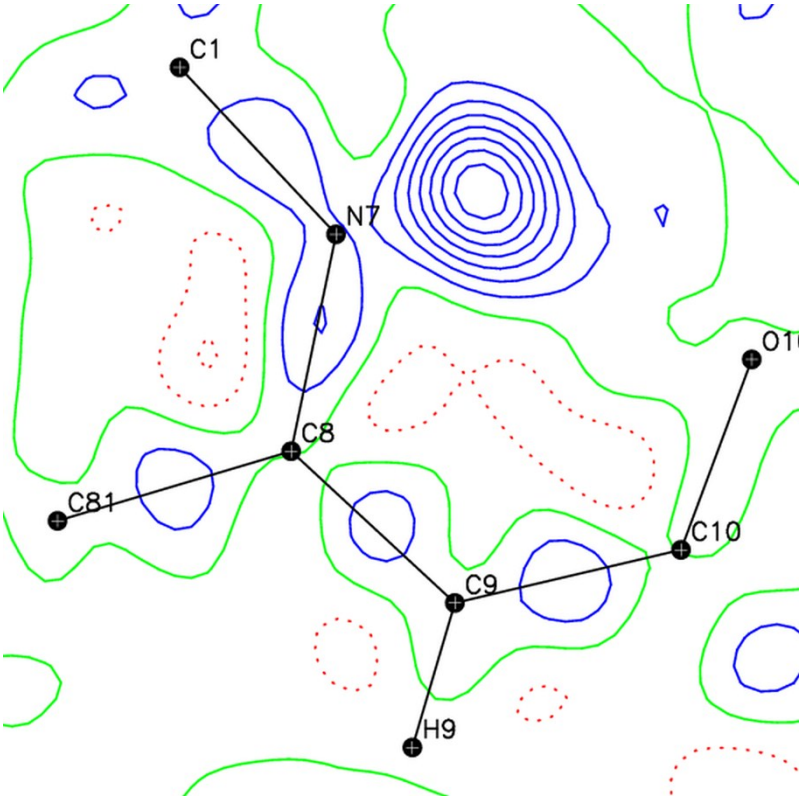


Figure 1S.

Table 3S. Selected geometrical data (Å,º) with s.u.'s in parentheses (second line, if exists, refers to alternative, less-occupied part). A and B denote least squares planes of aromatic ring and chain.

	3f	**5bA**	**5bB**	**5e**	**5g**
Ir1-N7		2.154(8)	2.171(6)	2.173(4)	2.153(3)
Ir1-O10		2.133(6)	2.152(6)	2.144(3)	2.133(3)
Ir1-N12		2.065(7)	2.037(6)	2.048(4)	2.037(3)
Ir1-C23		2.008(9)	2.006(8)	2.012(5)	1.970(3)
Ir1-N26		2.042(7)	2.045(6)	2.035(4)	2.049(3)
Ir1-C37		1.996(8)	2.016(8)	1.992(4)	2.012(3)
N7-Ir1-C23		173.3(3)	173.4(3)	175.18(15)	176.58(11)
O10-Ir1- C37		174.1(3)	175.2(3)	176.37(15)	175.58(11)
N12-Ir1-N26		176.2(3)	174.9(3)	175.34(15)	174.20(11)
C1-N7-C8	125.00(11)	118.3(8)	117.7(10) 119.9(13)	119.1(4)	119.1(3)
C13-N12-C25		120.1(8)	118.7(7)	118.1(4)	118.9(3)
C22-C23-C24		114.5(9)	115.5(8)	116.3(4)	114.0(3)
C27-N26-C39		119.3(7)	118.5(7)	118.0(4)	118.6(3)
C36-C37-C38		115.7(8)	115.8(7)	114.8(4)	116.2(3)
C2-C1-N7-C8	63.17(17)	-94.8(11)	-112.7(17) 78(3)	-72.5(6)	83.4(4)
C6-C1-N7-C8	-120.14(14)	87.2(10)	70(2) -107(3)	114.8(5)	-106.7(4)
C1-N7-C8-C9	-177.59(12)	-167.1(8)	-163.5(9) -177.2(9)	165.7(4)	-172.3(3)
C1-N7-C8-C81	4.93(19)	12.7(12)	13.6(12) 0.0(13)	-12.6(6)	9.1(5)
N7-C8-C9-C10	-0.6(2)	13.4(14)	15.3(14(	-16.4(8)	10.7(6)
C8-C9-C10-C11	-174.20(13)	165.6(8)	170.8(8)	-169.5(5)	173.9(3)
C8-C9-C10-O10	4.4(2)	-12.9(14)	-6.3(14)	6.8(8)	-5.3(6)
A/B	61.61(5)	74.2(5)	88.0(6) 88.0(8)	87.8(2)	88.40(13)

3. Thermal analysis data

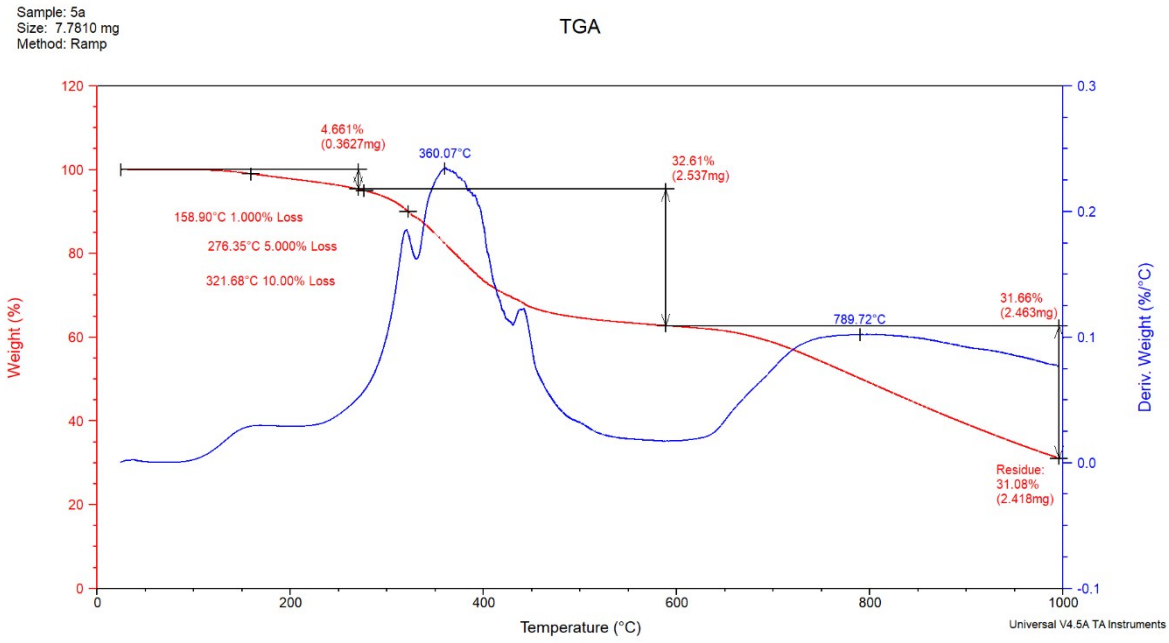


Figure 2S. TG and DTG curve of **5a** sample.

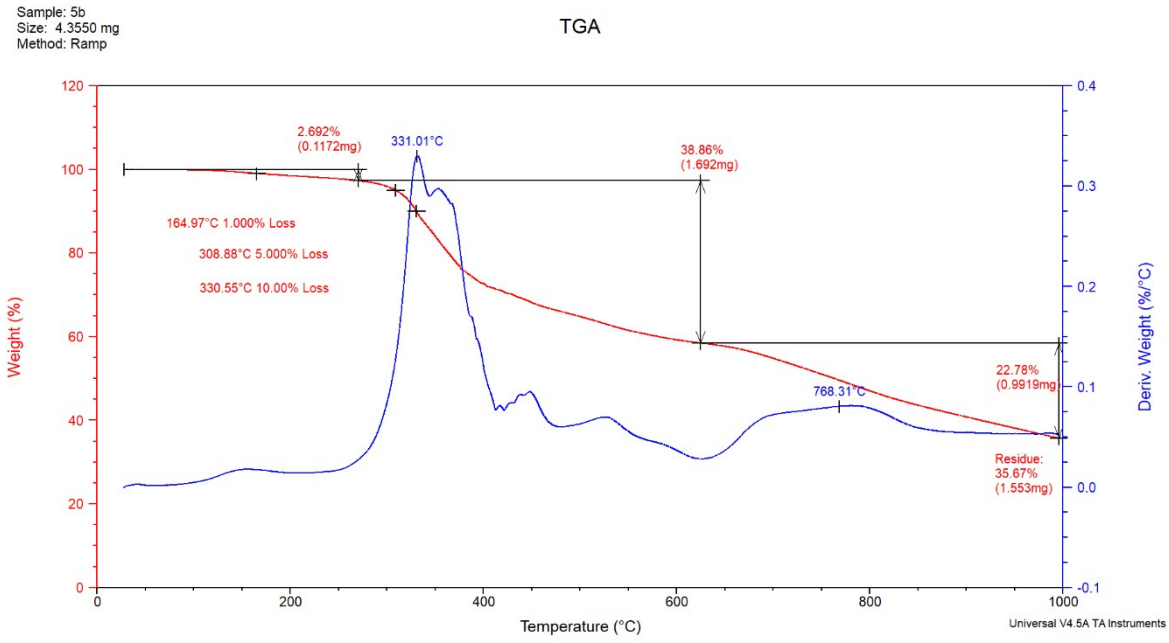


Figure 3S. TG and DTG curve of **5b** sample.

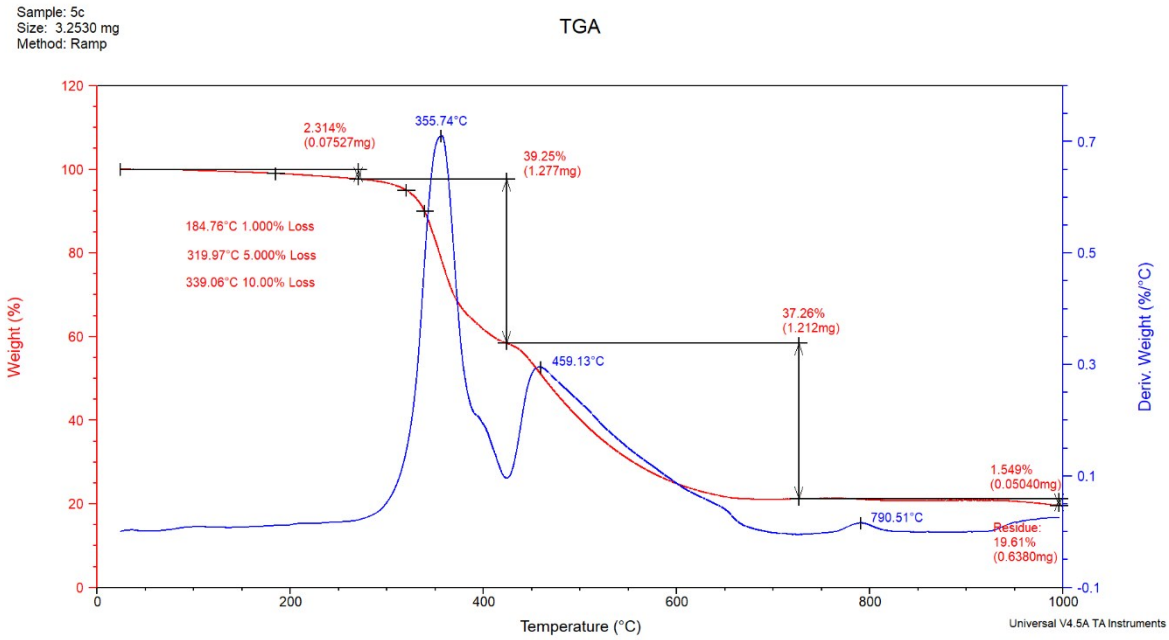


Figure 4S. TG and DTG curve of **5c** sample.

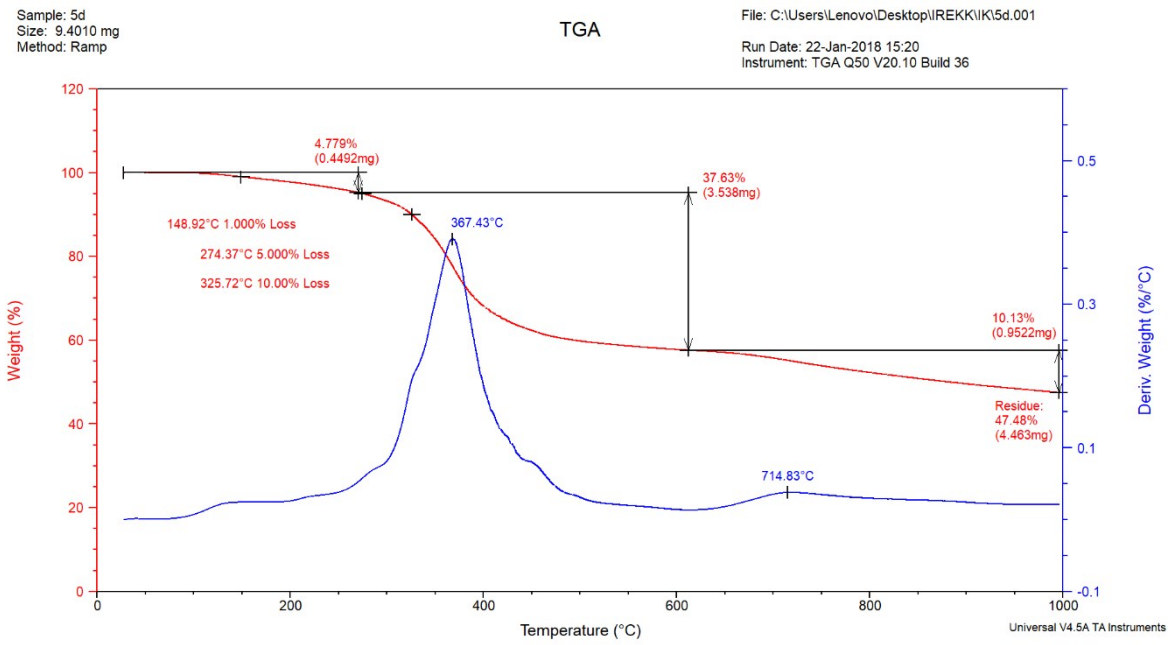


Figure 5S. TG and DTG curve of **5d** sample.

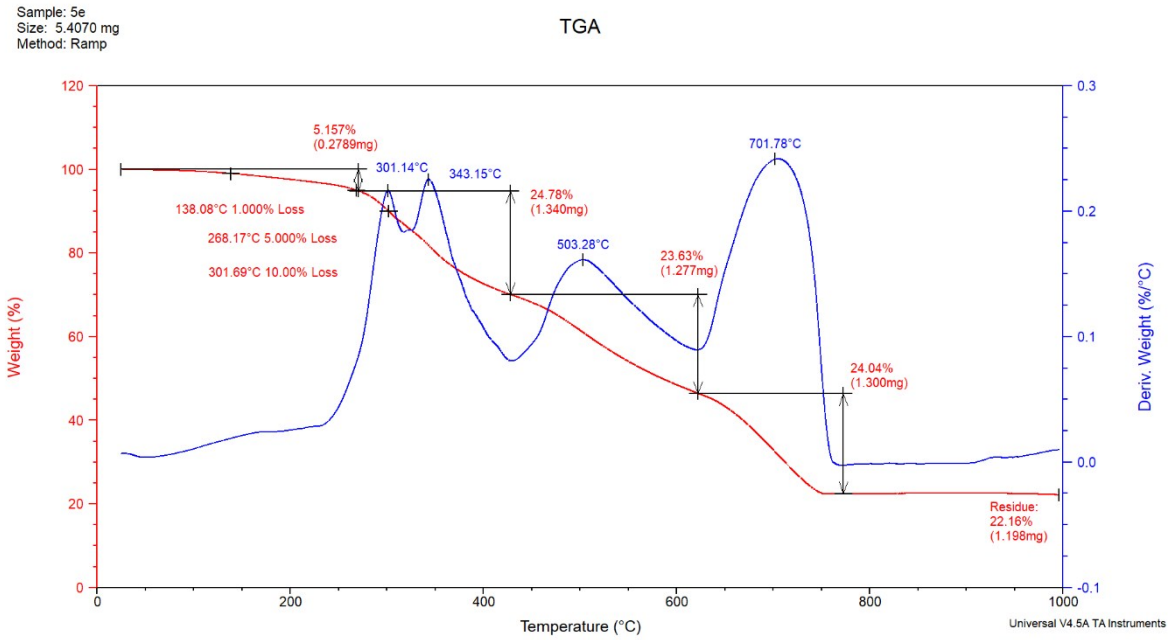


Figure 6S. TG and DTG curve of **5e** sample.

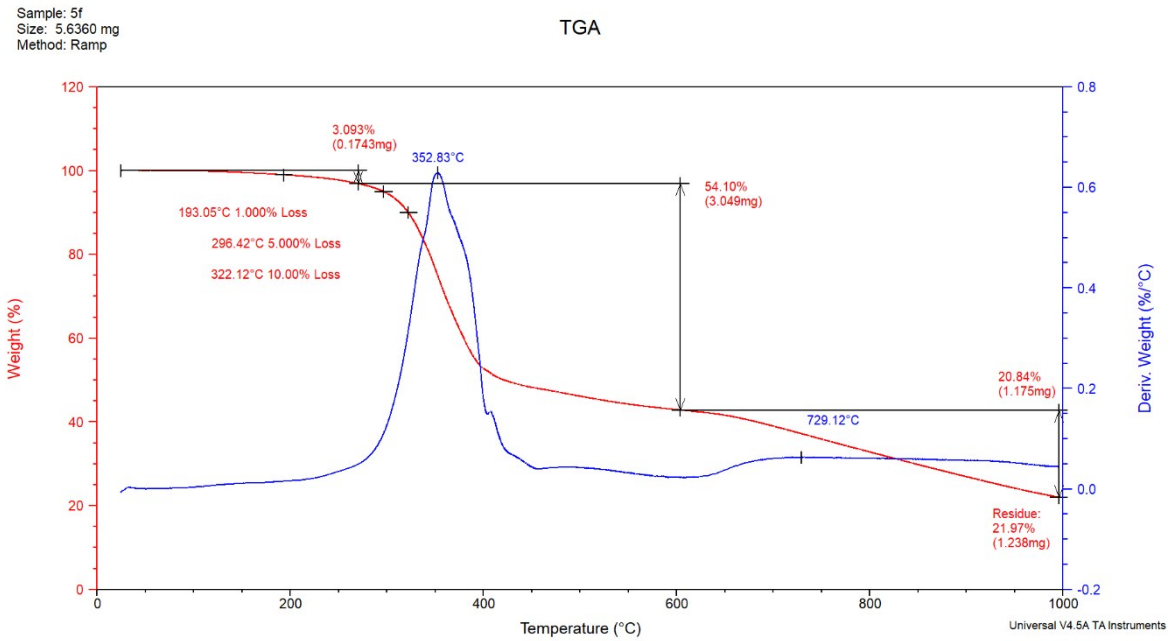


Figure 7S. TG and DTG curve of **5f** sample.

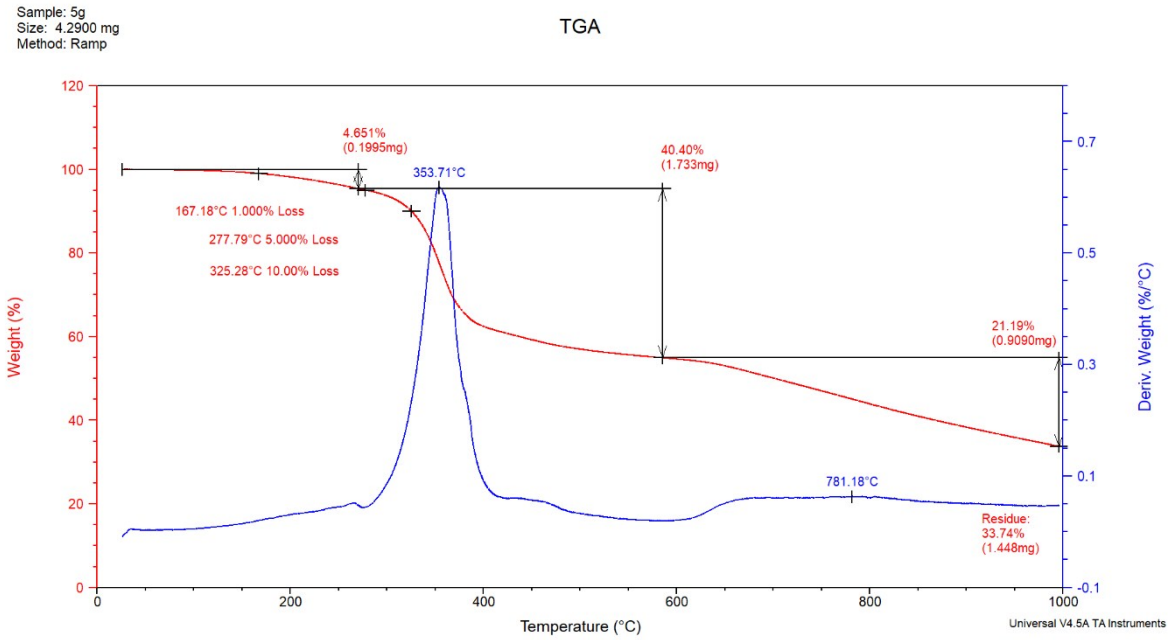


Figure 8S. TG and DTG curve of **5f** sample.

Table 4S. Results of TG and DTG analysis.

Sample	Weight Loss Temperature [°C]			Decomposition Temperature [°C]				Residue at 1000 °C [%]
	$T_{1\%}$	$T_{5\%}$	$T_{10\%}$	T_{Onset}	$T_{Max\ 1}$	$T_{Max\ 2}$	$T_{Max\ 3}$	
5a	159	276	322	286	360	-	790	31
5b	165	309	331	303	331	-	768	36
5c	185	320	339	328	356	459	791	20
5d	149	274	326	312	367	-	715	48
5e	138	268	302	268	301/343	503	702	22
5f	193	296	322	313	353	-	729	21
5g	167	278	325	319	354	-	781	34

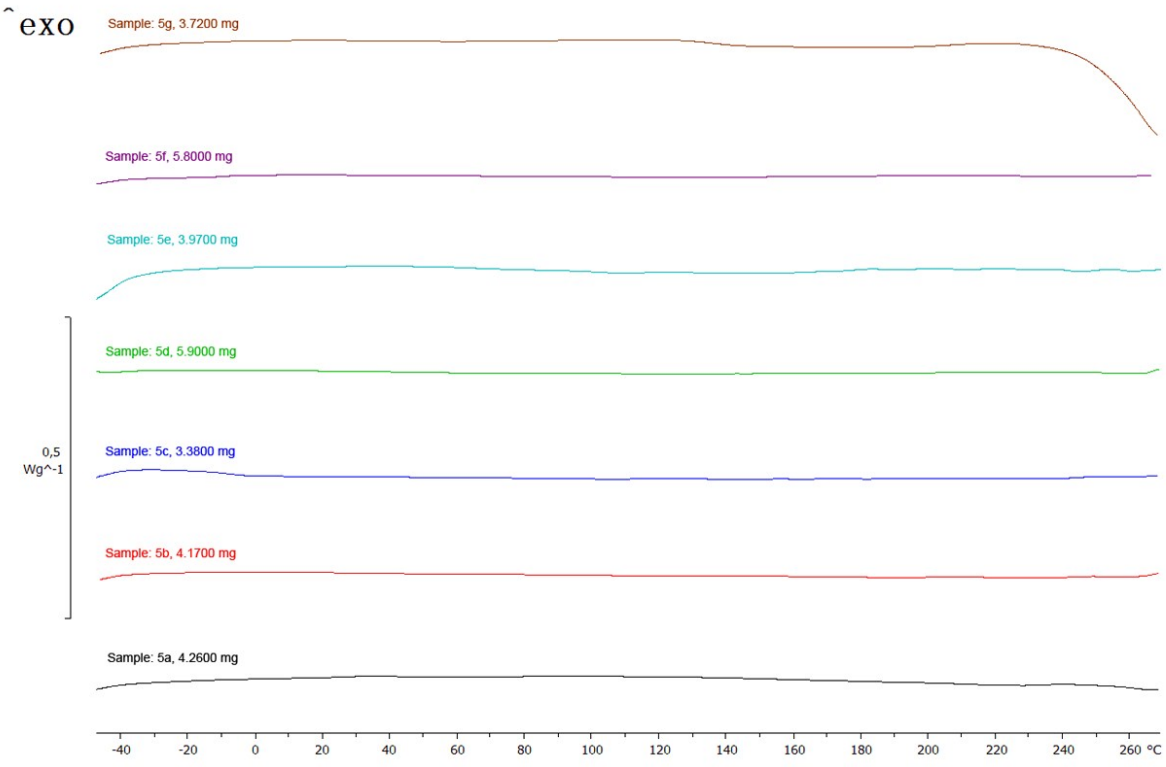


Figure 9S. DSC curves of second heating run for **5a**-**5g** samples.

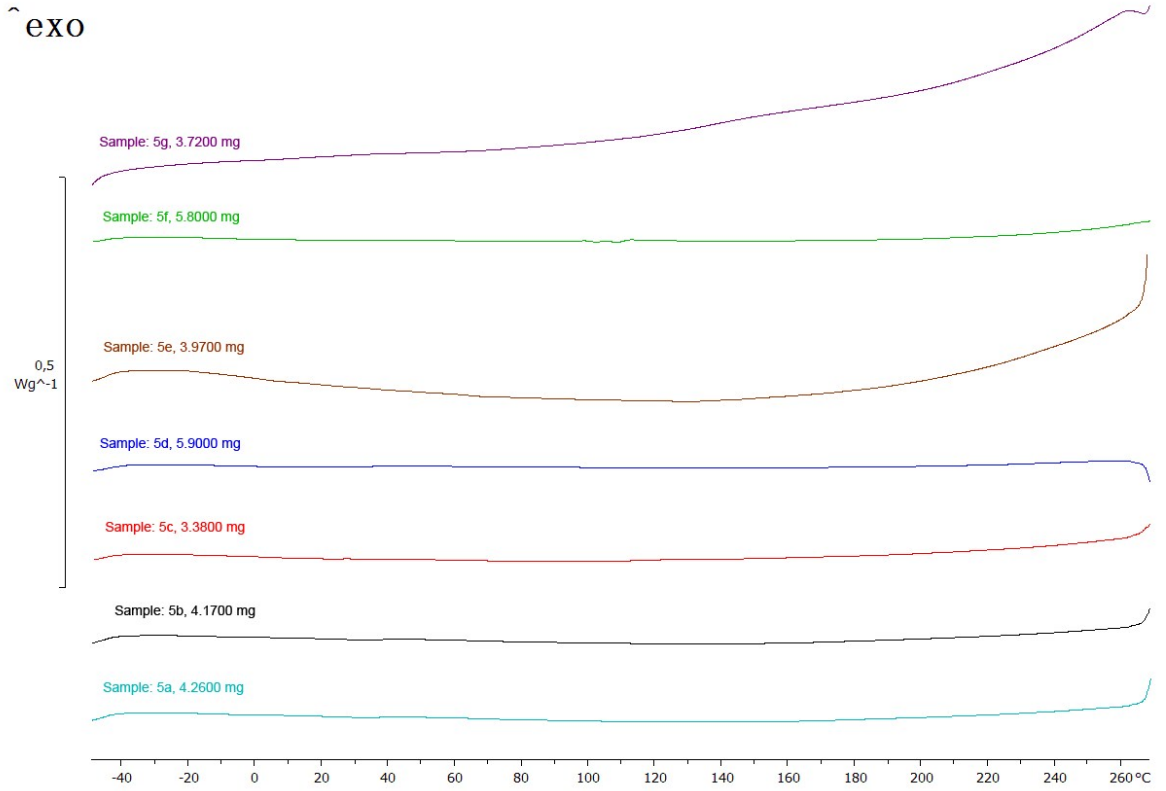


Figure 10S. DSC curves of second cooling run for **5a**-**5g** samples.

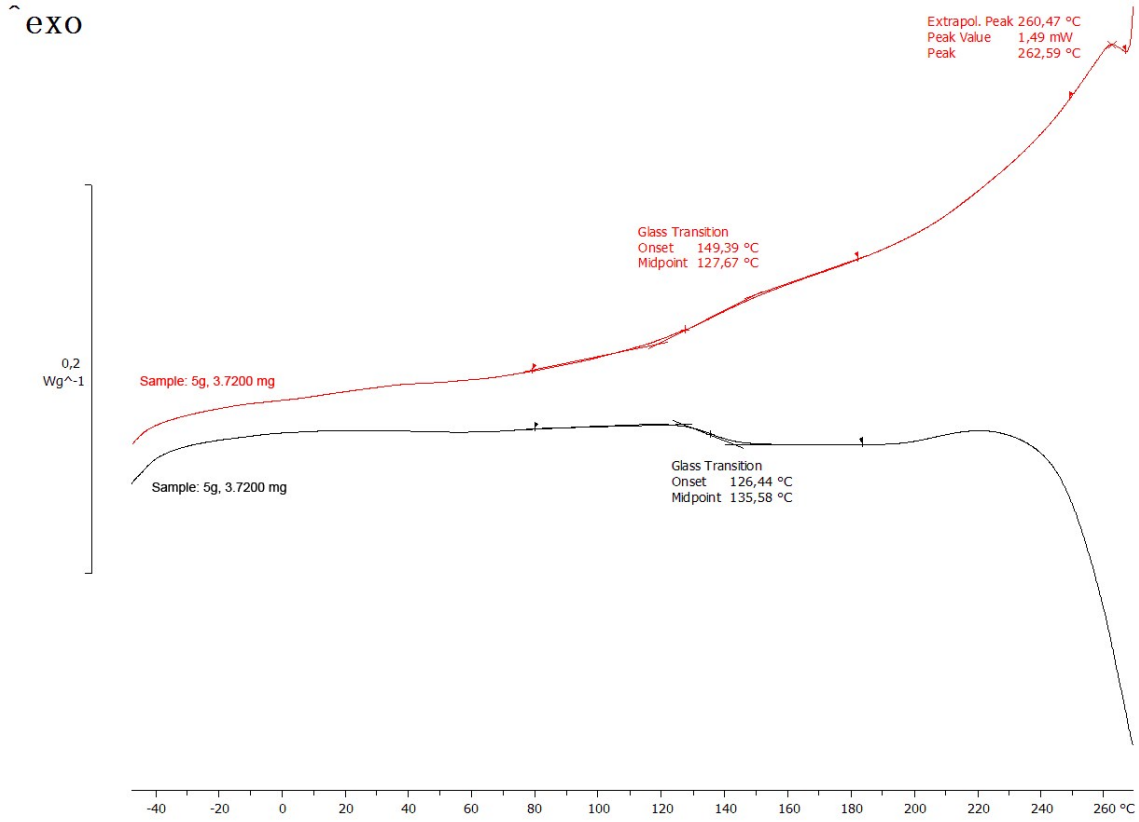


Figure 11S. DSC curves of second heating and cooling run for **5g** sample.

4. Cyclic voltammetry measurements

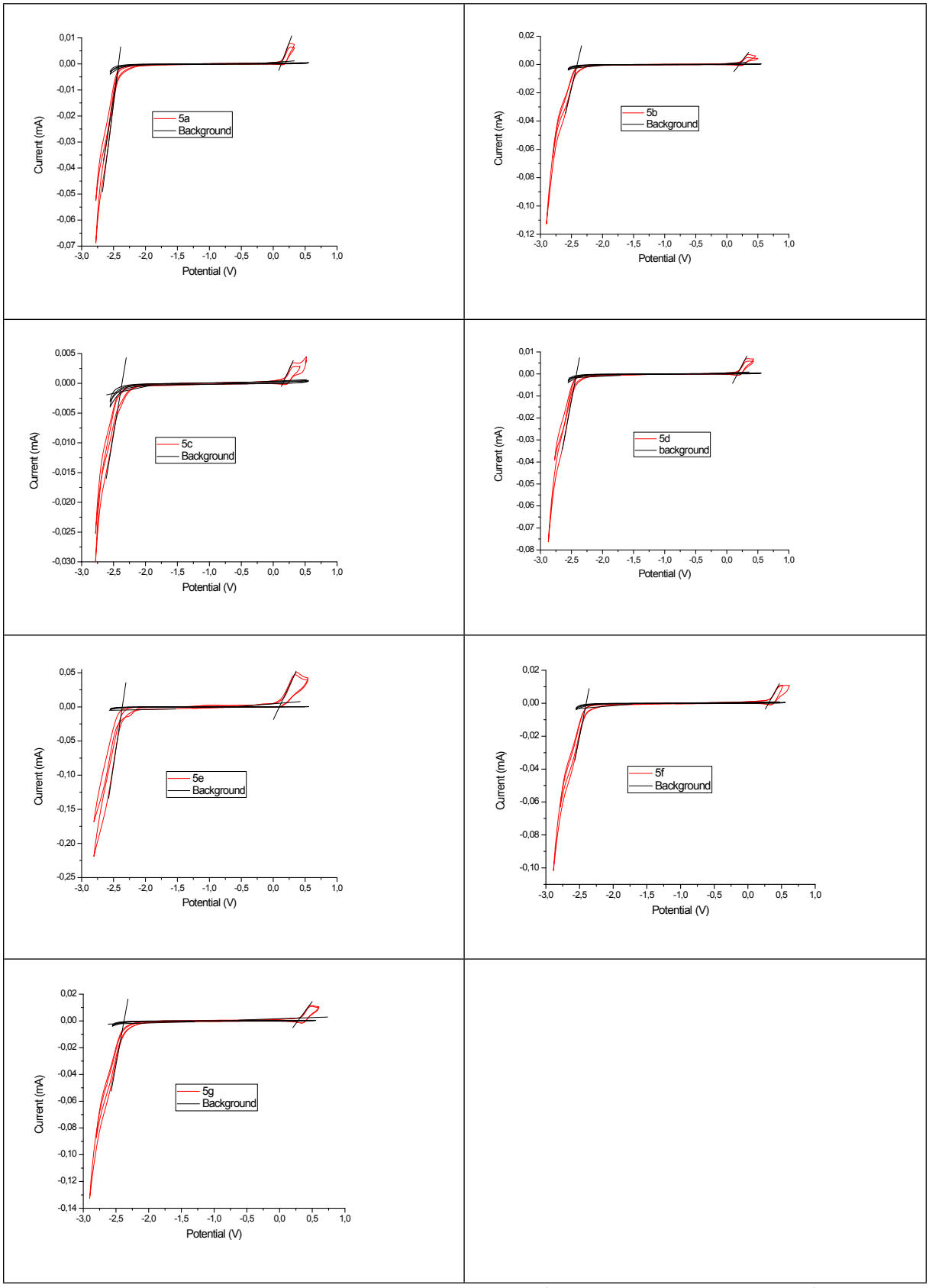


Figure 12S. Cyclic voltammetry of studied compounds in Bu_4NBF_4/CH_2Cl_2 solutions; scan rate 0.1V/s; concentration 2 mM. Intersections of tangential lines mark oxidation and reduction onset potentials.

5. DFT calculation data

Table 5S. The energy of optimized structures of iridium(II) complexes.

compound	Energy [hartree]
5a	-1771.23859192
5b$^{(1)}$	-1870.50717896
5b$^{(2)}$	-1870.50764600
5c$^{(1)}$	-1870.50889458
5c$^{(2)}$	-1870.50883848
5d	-1870.50778500
5e	-2108.39128637
5f	-2267.54834837
5g	-2436.72050752

Table 6S. The energy levels and Homo-Lumo energy gaps for the studied complexes (in eV) calculated at the B3LYP/SDD/6-311++G(d,p) level of theory together with the experimental results.

compound	HOMO [eV]	LUMO [eV]	$E_g^{theor.}$ [eV]	$E_g^{exp.}$ [eV]
5a	-5,28	-1,97	-3,31	2,58
5b$^{(1)}$	-5,32	-1,99	-3,33	2,63
5b$^{(2)}$	-5,30	-1,98	-3,32	2,63
5c$^{(1)}$	-5,32	-1,99	-3,33	2,57
5c$^{(2)}$	-5,32	-1,99	-3,33	2,57
5d	-5,30	-1,99	-3,31	2,62
5e	-5,36	-2,01	-3,34	2,48
5f	-5,43	-2,02	-3,41	2,73
5g	-5,38	-1,98	-3,41	2,69

Table 7S. The energy levels and Homo-Lumo energy gaps for the studied complexes (in eV) calculated at the M06/SDD/6-311++G(d,p) level of theory together with the experimental results.

compound	HOMO [eV]	LUMO [eV]	$E_g^{theor.}$ [eV]	$E_g^{exp.}$ [eV]
5a	-5,55	-1,86	-3,69	2,58
5b$^{(1)}$	-5,57	-1,88	-3,70	2,63
5b$^{(2)}$	-5,54	-1,88	-3,66	2,63
5c$^{(1)}$	-5,59	-1,88	-3,70	2,57
5c$^{(2)}$	-5,58	-1,89	-3,69	2,57
5d	-5,59	-1,89	-3,70	2,62
5e	-5,63	-1,92	-3,71	2,48
5f	-5,70	-1,92	-3,77	2,73
5g	-5,66	-1,91	-3,75	2,69

Table 8S. The energy levels and Homo-Lumo energy gaps for the studied complexes (in eV) calculated at the WB97XD/SDD/6-311++G(d,p) level of theory together with the experimental results.

compound	$E_g^{theor.}$ [eV]	$E_g^{theor.*}$ [eV]	$E_g^{exp.}$ [eV]
5a	6,87	2,61	2,58
5b	6,90	2,63	2,63
5c	6,89	2,62	2,57
5d	6,87	2,62	2,62
5e	6,63	2,52	2,48
5f	6,97	2,65	2,73
5g	6,96	2,64	2,69

$E_g^{thero^*}$= 0.38* $E_g^{theor.}$

Table 9S. Cartesian coordinates from the optimized structures of S_0 in C_6H_5Cl media for **5e**

Atom symbol	X	Y	Z
C	5.52148	0.57121	-2.15322
C	4.60221	1.28562	-1.30856
C	3.42613	0.62287	-0.87726
C	3.19118	-0.71972	-1.29067
C	4.10319	-1.41131	-2.12057
C	5.28690	-0.71451	-2.54224
N	2.03598	-1.29650	-0.83648
C	3.79057	-2.73741	-2.47212
C	2.62321	-3.30762	-1.99745
C	1.76991	-2.55769	-1.17891
C	4.80285	2.61504	-0.88238
C	3.85655	3.21875	-0.07025
C	2.69233	2.53899	0.34543
C	2.44582	1.22460	-0.04133
H	4.46516	-3.30215	-3.10640
H	2.35506	-4.32716	-2.24284
C	-1.05321	1.42853	-3.25269
C	-1.88374	2.41364	-2.74128
C	-0.21045	0.65959	-2.42381
C	-1.88412	2.66410	-1.35345
C	-2.69598	3.66905	-0.71999
C	-1.02788	1.88064	-0.54139
C	-2.65209	3.88646	0.62616
C	-1.78392	3.11500	1.47244
N	-0.12709	1.33509	1.57605
C	-1.66310	3.27936	2.86486
C	-0.02725	1.51238	2.89439
C	-0.78372	2.47684	3.57152
C	-0.17963	0.85339	-1.04446
H	-2.25436	4.03296	3.37366
H	0.67824	0.87299	3.40868
H	-0.66468	2.58189	4.64220
Ir	0.91375	-0.04132	0.41292
O	2.10731	-0.80624	2.08548
N	-0.58711	-1.61558	0.95576
C	1.93423	-1.92272	2.67961
C	0.83890	-2.78134	2.54852
C	-0.36588	-2.59324	1.82046

H	0.87730	-3.68080	3.14774
C	3.04521	-2.30618	3.63723
H	3.15819	-1.52486	4.39459
H	3.99131	-2.36288	3.09122
H	2.86230	-3.25886	4.13479
C	-1.44934	-3.62508	2.09133
H	-1.02528	-4.50377	2.57574
H	-1.95144	-3.93424	1.17300
H	-2.21596	-3.21429	2.75454
C	-0.98901	2.11998	0.86068
C	-1.89815	-1.46227	0.42260
C	-2.19010	-1.85788	-0.88834
C	-2.91016	-0.86713	1.18733
C	-4.18466	-0.68625	0.66317
C	-4.46544	-1.09463	-0.64178
C	-3.46377	-1.68458	-1.41543
H	-2.69089	-0.54181	2.19722
H	0.85573	-2.97767	-0.78290
H	5.99350	-1.23542	-3.17897
H	6.42221	1.07930	-2.48254
H	5.69168	3.15365	-1.19286
H	4.01199	4.24278	0.25531
H	1.98810	3.06658	0.97967
H	-1.04914	1.24236	-4.32245
H	0.41840	-0.09518	-2.88485
H	-2.52576	2.99255	-3.39632
H	-3.35628	4.26586	-1.34105
H	-3.27216	4.65126	1.08088
H	-3.67292	-1.99869	-2.43050
H	-1.41280	-2.30122	-1.49710
H	-4.95400	-0.22075	1.26692
C	-5.85097	-0.95035	-1.19037
F	-6.51153	0.11286	-0.67048
F	-6.63120	-2.03994	-0.92459
F	-5.86860	-0.80274	-2.53714

Table 10S. Cartesian coordinates from the optimized structures of S_0 in C_6H_5Cl media for **5a**.

Atom symbol	X	Y	Z
C	-5.13087	-1.75439	-0.73518
C	-3.92862	-2.08424	-0.01784
C	-2.84487	-1.17188	-0.05963
C	-2.97823	0.03526	-0.80396
C	-4.16643	0.34877	-1.50314
C	-5.24777	-0.59542	-1.44419
N	-1.89195	0.86826	-0.80074
C	-4.20955	1.56718	-2.20558
C	-3.10691	2.40174	-2.18295
C	-1.96501	2.02085	-1.46760
C	-3.76375	-3.26913	0.72934
C	-2.56545	-3.49660	1.38667
C	-1.49987	-2.57398	1.32889
C	-1.60768	-1.38743	0.60794
H	-5.10307	1.84429	-2.75437
H	-3.10755	3.34880	-2.70705
C	1.02043	-1.97794	-3.28502
C	2.11622	-2.68103	-2.80870
C	0.26475	-1.12499	-2.45490
C	2.48442	-2.54990	-1.45382
C	3.59532	-3.24058	-0.85469
C	1.70787	-1.69054	-0.63843
C	3.90642	-3.09427	0.46555
C	3.12888	-2.23844	1.31884
N	1.23305	-0.71845	1.46463
C	3.36853	-2.03735	2.69088
C	1.47874	-0.54612	2.76440
C	2.54150	-1.19082	3.40937
C	0.58991	-0.94637	-1.11185
H	4.19396	-2.54676	3.17632
H	0.80393	0.11445	3.29324
H	2.69735	-1.01819	4.46652
Ir	-0.29323	0.15171	0.34947
O	-1.19862	1.16275	2.06902
N	0.95791	1.98947	0.09734
C	-1.11158	2.41090	2.32893
C	-0.26558	3.33764	1.71712
C	0.75269	3.12250	0.74643

H	-0.33903	4.35092	2.08824
C	-2.02529	2.88680	3.44151
H	-1.81169	2.32255	4.35404
H	-3.06495	2.67967	3.17162
H	-1.91620	3.95168	3.64896
C	1.64303	4.32593	0.47768
H	1.17909	5.23486	0.85913
H	1.84350	4.44874	-0.58779
H	2.61035	4.20786	0.97389
C	2.03944	-1.55077	0.73821
C	2.11920	1.88948	-0.73275
C	2.01870	2.00244	-2.12365
C	3.37506	1.64640	-0.16423
C	4.50858	1.53820	-0.96841
C	4.40430	1.66732	-2.35299
C	3.15324	1.89731	-2.92551
H	3.45793	1.54396	0.91191
H	5.47390	1.35098	-0.51058
H	5.28541	1.58278	-2.97888
H	-1.08996	2.65377	-1.42419
H	-6.16400	-0.36543	-1.97696
H	-5.96034	-2.45355	-0.70275
H	-4.57185	-3.99065	0.78411
H	-2.44017	-4.40920	1.96147
H	-0.58584	-2.81168	1.86262
H	0.73357	-2.08625	-4.32672
H	-0.58252	-0.60305	-2.88715
H	2.68587	-3.33089	-3.46425
H	4.19394	-3.89526	-1.48012
H	4.74731	-3.62772	0.89529
H	1.04905	2.17380	-2.57504
H	3.05781	1.99197	-4.00176

Table 11S. Cartesian coordinates from the optimized structures of S_0 in C_6H_5Cl media for **5b**[1].

Atom symbol	X	Y	Z
C	5.31132	-1.55628	0.58307
C	4.10928	-1.92114	-0.11749
C	2.98210	-1.06831	-0.01464
C	3.07299	0.11551	0.77212
C	4.26099	0.46343	1.45516
C	5.38728	-0.42031	1.33359
N	1.94637	0.89125	0.82553
C	4.25996	1.65532	2.20288
C	3.11631	2.43228	2.23802
C	1.97796	2.02050	1.53428
C	3.98535	-3.08451	-0.90520
C	2.78324	-3.34958	-1.54103
C	1.67411	-2.48593	-1.42268
C	1.74113	-1.32183	-0.66150
H	5.15178	1.95754	2.74103
H	3.08219	3.35794	2.79802
C	-0.80386	-2.16649	3.25190
C	-1.88495	-2.88853	2.77094
C	-0.09220	-1.26058	2.43890
C	-2.28219	-2.72475	1.42756
C	-3.37739	-3.43503	0.82267
C	-1.55012	-1.81193	0.62934
C	-3.71144	-3.26038	-0.48855
C	-2.97588	-2.35310	-1.32585
N	-1.14021	-0.75951	-1.44904
C	-3.23624	-2.12606	-2.69028
C	-1.40355	-0.56511	-2.74145
C	-2.44686	-1.23349	-3.39395
C	-0.44923	-1.04672	1.10935
H	-4.04788	-2.65224	-3.18102
H	-0.76101	0.13455	-3.25977
H	-2.61899	-1.03969	-4.44483
Ir	0.36158	0.14093	-0.32321
O	1.19085	1.25735	-2.01576
N	-0.96876	1.91343	0.01816
C	1.02341	2.50124	-2.24694
C	0.13549	3.36383	-1.59759
C	-0.84295	3.07261	-0.61090
H	0.14128	4.38660	-1.94905
C	1.88173	3.05522	-3.36744
H	1.67359	2.50501	-4.28973

H	2.93735	2.89570	-3.12929
H	1.71133	4.11782	-3.54229
C	-1.78999	4.21666	-0.28952
H	-1.38044	5.16154	-0.64475
H	-1.98127	4.29454	0.78195
H	-2.75366	4.06381	-0.78431
C	-1.90648	-1.64163	-0.73811
C	-2.09094	1.73272	0.87493
C	-1.96421	1.72586	2.26959
C	-3.37138	1.50404	0.36414
C	-4.48223	1.29015	1.16344
C	-4.32678	1.29885	2.54802
C	-3.06408	1.51774	3.09779
F	-3.54583	1.50313	-0.98752
H	-5.44575	1.12161	0.69774
H	-5.18536	1.13281	3.18769
H	1.07204	2.61014	1.53408
H	6.30417	-0.16306	1.85258
H	6.17424	-2.20969	0.50352
H	4.82739	-3.76065	-1.00721
H	2.68923	-4.24587	-2.14660
H	0.75978	-2.75093	-1.94275
H	-0.49384	-2.30127	4.28384
H	0.74626	-0.72632	2.87359
H	-2.42020	-3.57946	3.41338
H	-3.94342	-4.12943	1.43545
H	-4.53864	-3.81071	-0.92352
H	-0.98352	1.88669	2.69933
H	-2.93261	1.52237	4.17352

Table 12S. Cartesian coordinates from the optimized structures of S_0 in C_6H_5Cl media for **5b²**.

Atom symbol	X	Y	Z
C	5.16794	1.62942	-0.98013
C	3.97405	2.07035	-0.31031
C	2.87795	1.17606	-0.22336
C	2.98961	-0.12251	-0.79802
C	4.16891	-0.54341	-1.45381
C	5.26412	0.38377	-1.52639
N	1.89184	-0.93232	-0.67836
C	4.19058	-1.84516	-1.98815
C	3.07568	-2.65126	-1.85264
C	1.94218	-2.16249	-1.19043
C	3.82867	3.34849	0.26841
C	2.63703	3.68119	0.89163
C	1.55912	2.77387	0.96537
C	1.64872	1.49849	0.41452
H	5.07719	-2.20556	-2.49863
H	3.05793	-3.65824	-2.24924
C	-1.10839	1.51046	-3.47668
C	-2.16743	2.31024	-3.07552
C	-0.33222	0.78245	-2.55151
C	-2.48118	2.40348	-1.70389
C	-3.55436	3.20536	-1.17892
C	-1.68774	1.66359	-0.79336
C	-3.81827	3.26901	0.15808
C	-3.02780	2.53113	1.10458
N	-1.16163	0.99895	1.41448
C	-3.22413	2.54011	2.49807
C	-1.36546	1.02656	2.73257
C	-2.39119	1.78679	3.30786
C	-0.60069	0.83108	-1.18498
H	-4.02130	3.13657	2.92837
H	-0.68704	0.43371	3.33221
H	-2.51393	1.77583	4.38324
Ir	0.32013	-0.04923	0.39474
O	1.27460	-0.82732	2.20822
N	-0.94851	-1.89451	0.44701
C	1.19476	-2.02593	2.63878
C	0.32693	-3.02448	2.18618
C	-0.72249	-2.93524	1.23377

H	0.40838	-3.97666	2.69227
C	2.14050	-2.35106	3.77842
H	1.95238	-1.66857	4.61245
H	3.17134	-2.18413	3.45289
H	2.03888	-3.37819	4.12967
C	-1.63429	-4.14868	1.15699
H	-1.21630	-4.97983	1.72307
H	-1.78675	-4.46855	0.12398
H	-2.62012	-3.91750	1.56961
C	-1.97322	1.73822	0.59856
C	-2.14587	-1.88537	-0.32423
C	-2.16932	-2.28025	-1.66263
C	-3.35704	-1.43552	0.21738
C	-4.52113	-1.38746	-0.54590
C	-4.50108	-1.78862	-1.88093
C	-3.31049	-2.24182	-2.44591
H	-3.36925	-1.12044	1.25422
H	-5.44202	-1.03317	-0.09742
H	-5.40179	-1.75036	-2.48187
H	1.05302	-2.76410	-1.07638
H	6.17366	0.07019	-2.02702
H	6.00712	2.31458	-1.04581
H	4.64676	4.05922	0.22109
H	2.52675	4.66615	1.33506
H	0.65208	3.09425	1.46668
H	-0.86658	1.44211	-4.53304
H	0.48484	0.17570	-2.92730
H	-2.75196	2.86222	-3.80369
H	-4.16346	3.77257	-1.87560
H	-4.63186	3.88237	0.52980
F	-1.02204	-2.75495	-2.22489
H	-3.25585	-2.56638	-3.47796

Table 13S. Cartesian coordinates from the optimized structures of S_0 in C_6H_5Cl media for **5c**[1].

Atom symbol	X	Y	Z
C	-5.33335	-1.52038	-0.78401
C	-4.15475	-1.91173	-0.05838
C	-3.02620	-1.05510	-0.08962
C	-3.09277	0.15867	-0.83186
C	-4.25746	0.53174	-1.54127
C	-5.38581	-0.35633	-1.49229
N	-1.96657	0.93679	-0.81713
C	-4.23272	1.75063	-2.24361
C	-3.08970	2.52871	-2.21087
C	-1.97545	2.09137	-1.48444
C	-4.05508	-3.10513	0.68675
C	-2.87462	-3.39459	1.35187
C	-1.76357	-2.52661	1.30482
C	-1.80710	-1.33428	0.58701
H	-5.10609	2.07191	-2.80065
H	-3.03778	3.47433	-2.73497
C	0.85540	-2.00803	-3.28745
C	1.91332	-2.76214	-2.80355
C	0.12301	-1.13381	-2.45857
C	2.26625	-2.66229	-1.44193
C	3.33826	-3.40552	-0.83477
C	1.51393	-1.78021	-0.62805
C	3.63506	-3.28707	0.49144
C	2.88132	-2.40851	1.34305
N	1.05075	-0.80974	1.47877
C	3.10878	-2.23284	2.72064
C	1.28311	-0.66355	2.78426
C	2.30730	-1.36052	3.43710
C	0.43473	-0.98527	-1.10874
H	3.90516	-2.78151	3.21164
H	0.62892	0.01872	3.31141
H	2.45437	-1.20659	4.49835
Ir	-0.41795	0.13995	0.35001
O	-1.29508	1.18660	2.06401
N	0.91985	1.92229	0.12707
C	-1.15334	2.42636	2.33477
C	-0.25802	3.31795	1.73838
C	0.76008	3.06175	0.78040
H	-0.28890	4.33108	2.11572

C	-2.05460	2.93603	3.44234
H	-1.86772	2.36290	4.35521
H	-3.09968	2.76842	3.16625
H	-1.90590	3.99558	3.65210
C	1.70989	4.22214	0.52869
H	1.27806	5.15268	0.89521
H	1.94140	4.33127	-0.53200
H	2.65803	4.06401	1.05041
C	1.83100	-1.66883	0.75472
C	2.08424	1.76561	-0.68309
C	2.01508	1.87632	-2.07688
C	3.31311	1.46090	-0.08477
C	4.42559	1.29226	-0.89128
C	4.38731	1.40844	-2.27027
C	3.15608	1.70441	-2.85614
H	3.40001	1.35606	0.98921
F	5.61641	0.99758	-0.29195
H	5.28506	1.26607	-2.85808
H	-1.07066	2.68010	-1.43192
H	-6.28491	-0.07928	-2.03178
H	-6.19732	-2.17674	-0.75886
H	-4.89875	-3.78530	0.73371
H	-2.79972	-4.31394	1.92462
H	-0.86656	-2.81120	1.84432
H	0.58036	-2.09234	-4.33455
H	-0.69508	-0.57181	-2.89703
H	2.46512	-3.42776	-3.45853
H	3.91856	-4.07743	-1.45909
H	4.44682	-3.85921	0.92714
H	1.06533	2.09687	-2.54662
H	3.08889	1.79749	-3.93390

Table 14S. Cartesian coordinates from the optimized structures of S_0 in C_6H_5Cl media for **5c²**.

Atom symbol	X	Y	Z
C	5.20959	1.34513	-1.32228
C	4.08502	1.86484	-0.59150
C	2.95878	1.02643	-0.39838
C	2.97503	-0.29565	-0.92812
C	4.08687	-0.79469	-1.64485
C	5.21385	0.07806	-1.82624
N	1.85472	-1.04907	-0.70239
C	4.01409	-2.11414	-2.12833
C	2.87789	-2.86402	-1.88421
C	1.81763	-2.29950	-1.16479
C	4.03618	3.16755	-0.05316
C	2.90515	3.57694	0.63442
C	1.79492	2.72480	0.81202
C	1.78968	1.42827	0.30446
H	4.84595	-2.53354	-2.68368
H	2.79049	-3.88383	-2.23616
C	-1.15870	1.45755	-3.42393
C	-2.18425	2.28755	-2.99814
C	-0.35886	0.73559	-2.51447
C	-2.43421	2.42326	-1.61693
C	-3.46459	3.26357	-1.06688
C	-1.61667	1.68979	-0.72260
C	-3.66244	3.37327	0.27855
C	-2.84159	2.64822	1.20905
N	-0.99565	1.08429	1.47704
C	-2.96639	2.70778	2.60948
C	-1.13110	1.16016	2.80185
C	-2.10930	1.96283	3.40163
C	-0.56932	0.81989	-1.13970
H	-3.72792	3.33603	3.05866
H	-0.43555	0.57149	3.38572
H	-2.17706	1.99041	4.48158
Ir	0.39180	-0.05271	0.42103
O	1.39943	-0.80099	2.21899
N	-0.94472	-1.83831	0.59784
C	1.28549	-1.97647	2.70441
C	0.35687	-2.95104	2.33030
C	-0.72919	-2.85365	1.41871
H	0.42193	-3.88749	2.86762

C	2.26432	-2.29714	3.81702
H	2.13065	-1.58293	4.63494
H	3.28676	-2.17563	3.44803
H	2.14233	-3.30835	4.20609
C	-1.68216	-4.03860	1.43143
H	-1.19755	-4.90829	1.87427
H	-2.02401	-4.29484	0.42777
H	-2.57054	-3.81180	2.02770
C	-1.83167	1.81451	0.67824
C	-2.17105	-1.80302	-0.13034
C	-2.18954	-2.09206	-1.49955
C	-3.36501	-1.43546	0.50367
C	-4.55678	-1.37028	-0.21432
C	-4.58730	-1.66347	-1.57749
C	-3.39168	-2.01746	-2.18047
H	-3.35173	-1.19908	1.56079
H	-5.47287	-1.08453	0.28974
H	-5.50037	-1.61529	-2.15690
H	0.92016	-2.86262	-0.94934
H	6.07251	-0.29411	-2.37428
H	6.07158	1.98790	-1.46984
H	4.87992	3.83709	-0.18110
H	2.86915	4.58053	1.04722
H	0.93815	3.10449	1.35842
H	-0.96417	1.35865	-4.48754
H	0.42886	0.10282	-2.91010
H	-2.78944	2.83273	-3.71441
H	-4.09430	3.82308	-1.75131
H	-4.44437	4.01528	0.66930
H	-1.28631	-2.36582	-2.02754
F	-3.39378	-2.30892	-3.51398

Table 15S. Cartesian coordinates from the optimized structures of S_0 in C_6H_5Cl media for **5d**.

Atom symbol	X	Y	Z
C	-5.27241	-1.40587	-1.22496
C	-4.15967	-1.85311	-0.43088
C	-3.02392	-1.01193	-0.32467
C	-3.02066	0.24278	-0.99849
C	-4.12133	0.67134	-1.77565
C	-5.25740	-0.20355	-1.86821
N	-1.89325	1.00448	-0.84804
C	-4.02967	1.92869	-2.40077
C	-2.88716	2.68929	-2.23013
C	-1.83868	2.19646	-1.44381
C	-4.13147	-3.08675	0.25226
C	-3.01104	-3.42842	0.99228
C	-1.89106	-2.57515	1.08096
C	-1.86478	-1.34539	0.42861
H	-4.85251	2.29288	-3.00629
H	-2.78613	3.66344	-2.69105
C	1.06937	-1.82447	-3.27706
C	2.07899	-2.62420	-2.76418
C	0.28698	-0.99062	-2.45201
C	2.33024	-2.61305	-1.37652
C	3.34433	-3.40991	-0.73855
C	1.53015	-1.76915	-0.56784
C	3.54393	-3.37561	0.61065
C	2.74182	-2.53490	1.45621
N	0.92881	-0.91427	1.55372
C	2.87080	-2.44256	2.85451
C	1.06858	-0.84549	2.87848
C	2.03275	-1.59716	3.56145
C	0.49881	-0.92869	-1.07620
H	3.62100	-3.03375	3.36840
H	0.38740	-0.18103	3.39405
H	2.10455	-1.50703	4.63771
Ir	-0.44503	0.11946	0.38260
O	-1.43236	1.06738	2.09517
N	0.92040	1.88959	0.36468
C	-1.31125	2.29239	2.43600
C	-0.37889	3.21026	1.94693
C	0.71207	2.99534	1.06026
H	-0.43718	4.20408	2.36977

C	-2.28405	2.74735	3.50633
H	-2.14831	2.13574	4.40329
H	-3.30868	2.58559	3.15955
H	-2.15740	3.79741	3.77114
C	1.68284	4.16049	0.94666
H	1.22011	5.07658	1.31242
H	2.01121	4.31434	-0.08231
H	2.57886	3.97575	1.54610
C	1.74725	-1.74427	0.83819
C	2.15630	1.75898	-0.34231
C	2.21301	1.92442	-1.73060
C	3.32902	1.42198	0.34393
C	4.53809	1.26731	-0.33231
C	4.55350	1.45058	-1.70428
C	3.41415	1.77624	-2.42082
H	3.29420	1.27834	1.41736
H	5.44906	1.00636	0.19221
F	5.73313	1.30075	-2.37597
H	-0.93639	2.77016	-1.28333
H	-6.10764	0.11494	-2.46142
H	-6.14145	-2.05095	-1.30633
H	-4.98277	-3.75642	0.19367
H	-2.99138	-4.37851	1.51751
H	-1.04287	-2.90059	1.67383
H	0.87289	-1.83970	-4.34493
H	-0.48940	-0.39021	-2.91460
H	2.67038	-3.25738	-3.41674
H	3.95989	-4.05419	-1.35822
H	4.31289	-3.98778	1.06918
H	1.31201	2.17226	-2.27713
H	3.46634	1.90536	-3.49485

Table 16S. Cartesian coordinates from the optimized structures of S_0 in C_6H_5Cl media for **5f**.

Atom symbol	X	Y	Z
C	5.59389	0.77833	-1.59357
C	4.53184	1.49229	-0.93727
C	3.35155	0.78526	-0.59748
C	3.25228	-0.59984	-0.91368
C	4.30514	-1.29060	-1.55564
C	5.48933	-0.54862	-1.88935
N	2.08358	-1.21784	-0.55751
C	4.12306	-2.66107	-1.81807
C	2.94179	-3.27201	-1.44018
C	1.94286	-2.51977	-0.80954
C	4.59606	2.86268	-0.60919
C	3.51977	3.46153	0.02457
C	2.35482	2.73695	0.35417
C	2.23947	1.38201	0.05699
H	4.90729	-3.22658	-2.30950
H	2.76986	-4.32500	-1.62228
C	-0.87082	1.07063	-3.55149
C	-1.79956	2.04758	-3.22941
C	-0.08820	0.43298	-2.56607
C	-1.96858	2.42341	-1.88041
C	-2.89516	3.43181	-1.43854
C	-1.17252	1.76922	-0.90841
C	-3.01575	3.77082	-0.12261
C	-2.21538	3.12927	0.88378
N	-0.50186	1.46145	1.33895
C	-2.26425	3.42276	2.25951
C	-0.56465	1.75936	2.63709
C	-1.43654	2.73739	3.13131
C	-0.22027	0.75565	-1.21749
H	-2.94576	4.18246	2.62633
H	0.09965	1.20486	3.28683
H	-1.44884	2.94170	4.19410
Ir	0.73847	0.05650	0.42924
O	1.73547	-0.51964	2.29686
N	-0.74991	-1.55961	0.90768
C	1.53026	-1.58736	2.95815
C	0.49531	-2.51586	2.76245
C	-0.60494	-2.45767	1.87935
H	0.49371	-3.35691	3.44189

C	2.51267	-1.83273	4.08556
H	2.48704	-0.98601	4.77754
H	3.52602	-1.88354	3.67723
H	2.30284	-2.74914	4.63717
C	-1.67366	-3.51441	2.08905
H	-1.30608	-4.30771	2.73806
H	-1.99386	-3.95648	1.14308
H	-2.55673	-3.07748	2.56477
C	-1.30855	2.13209	0.46139
C	-1.98219	-1.50480	0.22032
C	-2.12844	-1.98711	-1.08398
C	-3.10973	-0.89114	0.77751
C	-4.30174	-0.74828	0.08125
C	-4.40358	-1.22575	-1.21754
C	-3.31025	-1.85237	-1.79864
F	-3.05654	-0.42128	2.03680
F	-5.35553	-0.14921	0.65625
H	1.00855	-2.96910	-0.50716
H	6.30290	-1.06898	-2.38283
H	6.49747	1.32020	-1.85385
H	5.48365	3.43591	-0.85439
H	3.57086	4.51664	0.27524
H	1.54585	3.26268	0.84959
H	-0.73870	0.78672	-4.59100
H	0.62423	-0.32145	-2.88125
H	-2.39092	2.52596	-4.00259
H	-3.50785	3.93140	-2.18211
H	-3.71935	4.53613	0.18621
F	-1.10872	-2.63286	-1.67427
F	-3.40442	-2.33394	-3.04683
F	-5.54733	-1.08867	-1.90134

Table 17S. Cartesian coordinates from the optimized structures of S_0 in C_6H_5Cl media for **5g**.

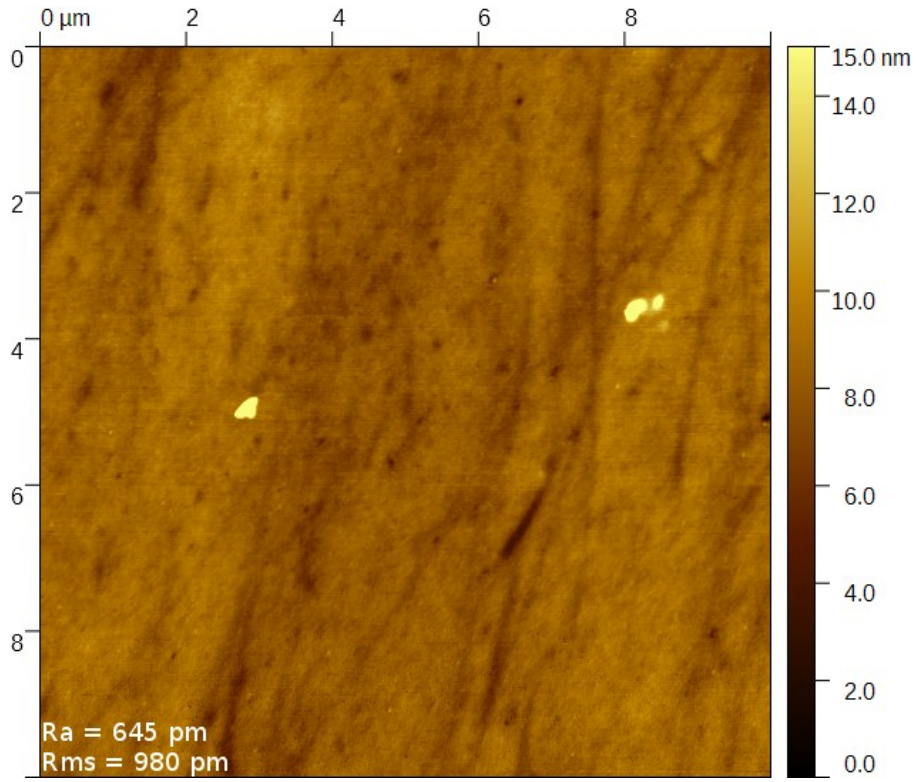
Atom symbol	X	Y	Z
C	5.80545	-0.97235	-2.49982
C	5.02042	0.14016	-2.03675
C	3.85608	-0.12568	-1.27387
C	3.49794	-1.47542	-0.99390
C	4.27912	-2.55973	-1.45381
C	5.45538	-2.26075	-2.22270
N	2.35809	-1.65718	-0.25747
C	3.85211	-3.85926	-1.12350
C	2.70457	-4.02418	-0.37036
C	1.98175	-2.89949	0.04737
C	5.34250	1.48825	-2.29894
C	4.52212	2.49114	-1.80907
C	3.36817	2.20233	-1.05034
C	3.00546	0.89039	-0.75889
H	4.42362	-4.71781	-1.45914
H	2.34851	-5.00873	-0.09569
C	-0.82234	-0.03251	-3.45045
C	-1.50047	1.17583	-3.41797
C	0.05202	-0.42431	-2.41514
C	-1.31380	2.04438	-2.32249
C	-1.95941	3.32389	-2.19284
C	-0.43368	1.62866	-1.29347
C	-1.74163	4.13415	-1.11704
C	-0.85135	3.73917	-0.06031
N	0.64952	2.01330	0.77298
C	-0.56046	4.51191	1.07950
C	0.90843	2.76390	1.84424
C	0.31975	4.02097	2.02785
C	0.26632	0.38841	-1.30448
H	-1.02465	5.48379	1.20699
H	1.60308	2.34827	2.56245
H	0.56438	4.59131	2.91464
Ir	1.45129	0.14417	0.32645
O	2.75154	0.08233	2.09179
N	-0.10363	-0.82584	1.62869
C	2.55044	-0.59455	3.15071
C	1.37822	-1.28040	3.50262
C	0.12803	-1.31432	2.84395
H	1.40842	-1.79157	4.45496

C	3.71520	-0.61565	4.12033
H	3.95920	0.40923	4.41468
H	4.59656	-1.02434	3.61812
H	3.50832	-1.20277	5.01517
C	-1.00300	-1.96555	3.61911
H	-0.61372	-2.52396	4.46909
H	-1.58259	-2.64423	2.98980
H	-1.68976	-1.20648	4.00495
C	-0.21630	2.48260	-0.17591
C	-1.44057	-0.77096	1.17216
C	-1.93908	-1.65433	0.21143
C	-2.32771	0.22172	1.60140
C	-3.61418	0.33481	1.09763
C	-4.09928	-0.55130	0.13423
C	-3.22720	-1.55308	-0.29387
F	-1.93138	1.10612	2.53879
F	-4.40952	1.32950	1.54033
O	-5.33211	-0.42108	-0.42394
H	1.07792	-2.99627	0.63032
H	6.06194	-3.08569	-2.58011
H	6.69754	-0.76840	-3.08331
H	6.22577	1.72928	-2.88058
H	4.77097	3.52803	-2.01333
H	2.76564	3.03143	-0.69540
H	-0.96569	-0.69801	-4.29614
H	0.55723	-1.38036	-2.49870
H	-2.16893	1.45767	-4.22426
H	-2.63547	3.64283	-2.97971
H	-2.23865	5.09519	-1.04261
F	-1.16646	-2.66830	-0.22331
F	-3.64138	-2.44413	-1.21073
C	-6.45114	-0.78633	0.42420
C	-7.72658	-0.62357	-0.36444
H	-6.47631	-0.13026	1.29839
H	-6.33064	-1.82377	0.74988
O	-7.82455	-1.64983	-1.33620
H	-7.74325	0.36591	-0.84261
H	-8.57411	-0.67567	0.33532
C	-8.97915	-1.52403	-2.15254
H	-8.96461	-2.35262	-2.86025
H	-8.97253	-0.57677	-2.70701
H	-9.89829	-1.57774	-1.55391

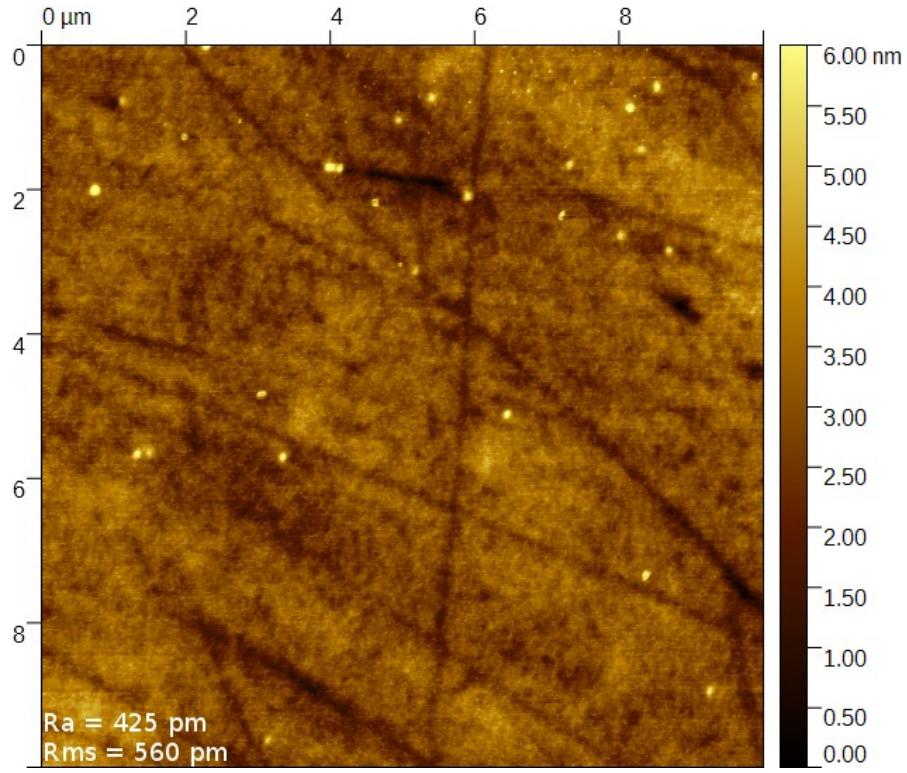
6. AFM data

Images of thin layers:

5 wt% of complex **5g** in PVK:PBD matrix



0.5 wt% of complex **5g** in PVK:PBD matrix


0 µm
2
4
6
8
0
2
4
6
8
6.00 nm
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
Ra = 425 pm
Rms = 560 pm